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LOW VOLTAGE, HIGH RESISTANCE,
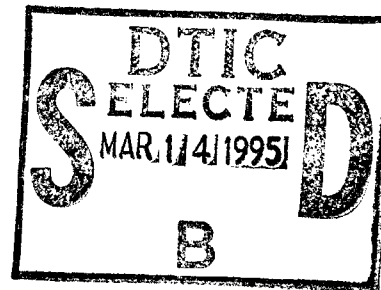POLYMER DISPERSED LIQUID CRYSTAL

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PATRICK MULLEN (PEREGRINE)

MAGNASCREEN CORPORATION
265 KAPPA DRIVE
PITTSBURGH, PA   15238

MARCH 1994

FINAL REPORT FOR 09/01/92-03/01/94

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AVIONICS DIRECTORATE
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AIR FORCE MATERIEL COMMAND
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13. ABSTRACT (Maximum 200 words)

This document presents the results of the development of a low voltage, high resistivity, dyed Polymer Dispersed Liquid Crystal (PDLC) for use in direct view displays. Several methods for improving various PDLC characteristics are described. The optimized PDLC formulation shows substantial improvement in all operational characteristics with the single exception of hysteresis, which remains unacceptably high. Alternative applications of developed PDLC materials are discussed.

14. SUBJECT TERMS
PDLC, Dyed PDLC, Low Voltage PDLC, Hysteresis, Characterization of PDLC, Flat Panel, Direct View, Active Matrix Display

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SUMMARY OF PROPRIETARY CLAIMS

Magnascreen's proprietary claims on results, prototypes, or systems that are supporting, and/or necessary for research results, and/or prototypes, include:

- Modular display systems utilizing dyed PDLC material for light modulation in direct view mode.

- Modular display systems utilizing PDLC material for light modulation in projection mode.

Peregrine's proprietary claims on results, prototypes, or systems that are supporting, and/or necessary for research results, and/or prototypes, include:

- Polymers containing silicon as PDLC matrices.

- Unique switching circuit for fast switching PDLC's.

- Viscosity reducing agents which reduce PDLC drive voltage.

To assure maximum opportunity for financial success in their business, Peregrine wishes to retain rights to present and future proprietary materials, processes and hardware that may be involved in this program, including:

- All patents already applied for by Peregrine,

- All disclosures in Peregrine's figuring books not yet filed, and,

- All patentable items arising from the proposed work, whether filed during the period of the contract, or afterward.

Peregrine, under suitable circumstances and appropriate terms, is willing to license the technologies developed to other companies. Specifically, Peregrine has an interest in developing arrangements with suitable Liquid Crystal Display (LCD) manufacturers who can implement Peregrine's proprietary processes for LCD fabrication.

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1.   INTRODUCTION

1.1 BACKGROUND

The need for large area, high resolution, direct view display systems continues to exist for both commercial and military applications. These applications require luminance and contrast sufficient for viewing in varied ambient lighting conditions, image linearity, and the relatively thin profile of "a picture on the wall" impossible to obtain with projection systems.

LCD continues to be one of the best potential solutions for direct view, large area display systems. However, processing difficulties currently and for the foreseeable future limit display size to well below the minimum goal of 1 meter diagonal.

One solution for providing a large area LCD system is to tile arrays of smaller manufacturable display units (LCD modules) to create a tiled, large area display that is "seamless" in appearance.

Magnascreen, under a previous DARPA Contract (MDA972-90-C-0032), addressed the important issues of tiled LC displays. Results of that effort suggested that the need to seal the liquid crystal within each module (using an epoxy seal of a finite width along the periphery of the module) limits the achievable pixel density of the display.

Polymer Dispersed Liquid Crystal (PDLC), which contains tiny droplets of liquid crystal in a solidified polymer base, is a self-sealing display medium and thus does not require a seal at the periphery of the display module.

Within the framework of Contract MDA972-90-C-0032 the seamless appearance of a tiled display was demonstrated by tiling four display modules which employed a PDLC medium laminated on customary active matrix substrates. However, the electro-optic (EO) performance of the PDLC was unsatisfactory, resulting in poor contrast and low brightness.

Magnascreen Corporation was awarded, in September 1992, Contract F3361-92-C-1097 to develop, in cooperation with Peregrine Optifilm, Inc., a PDLC formulation suitable for application in Magnascreen's tiled, large area, high resolution, direct view display system.

1.2 PROGRAM OBJECTIVE

The program objective was to

- develop a dyed PDLC formulation suitable for use in a direct view, high definition, large area, tiled display system.

- develop a process for manufacturing PDLC displays without edge seal areas.

- demonstrate improved PDLC electro-optical performance.

The existing PDLC performance parameters before the start of the program and the target performance specification developed for this program are shown in Table 1.

TABLE 1. Performance Goals

	INITIAL*	TARGET
Operational Voltage (V_{90})	60-80 V_{rms}	< 15 V_{rms}
Response Times (t_{ON}, t_{OFF})	50-100 ms	< 20 ms
Contrast Ratio (direct view)	2 : 1	> 8 : 1
Transmittance (@ V_{90})	30-40%	> 60%
Resistivity (DC, aged)	10^{10}-10^{11} Ωcm	> 10^{12} Ωcm
Hysteresis (δV_H)	5-10 V	< 0.1 V
Temperature Range	unknown	-30° to +70°C
Uniformity (of EO performance)	± 4%	± 2%
Stable to edge	no	yes

*Initial values indicate performance of typical PDLC formulations available to Magnascreen prior the initiation of this program.

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The importance of each parameter for the display performance is briefly discussed below. For definition of parameters see Appendix A.

Operating Voltage

The PDLC materials (available to Magnascreen prior to initiation of this program) required driving voltage of 60 to 80 V. The commercially available active matrices (AM) cannot sustain such high voltage without severe degradation of their performance. The target value of 15 V was chosen as Magnascreen learned about the availability of customized AM with an operating voltage of 15-20 V (Xerox-PARC).

Response Times

Fast response times (t_{ON}, t_{OFF}) to sudden changes in driving signal amplitude is required of any display medium to be a suitable candidate for video applications. A value of 20 ms guarantees an excellent video performance.

Contrast Ratio

Contrast ratio (C/R) of 30:1 or better is required for good color rendition and multilevel gray scale. Because such a goal appeared unrealistic at the onset of the program, the C/R of 8:1 was chosen for the target value; such a contrast ratio would result in satisfactory monochrome performance.

Transmittance

The ON transmittance of the PDLC influences the ultimate brightness of the display. The 60% of the ON transmittance (at V_{90}) would provide brighter displays than the standard LC technology utilizing polarizers (a typical LCD ON transmittance is 40%).

Resistivity

The direct current (DC) resistivity has a very strong effect on quality of displayed images using AM addressing of LCD. To prevent a noticeable degradation of the contrast ratio during a single frame time, a voltage holding ratio of 97.5% is required. At a refresh rate of 60 Hz this is equivalent to a DC resistivity of 10^{12} Ω.cm (see also page 56).

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Hysteresis

The hysteresis observed on the transmittance-voltage (T-V) characteristics of PDLC (i.e. difference between upward and downward sweeps) has an adverse effect on gray scale accuracy, color rendition and, in severe cases, can cause "image sticking". The hysteresis of 0.1 V was shown to mitigate the problems to a negligible level.

Temperature Range

The -30 to +70 °C was adopted as a minimum requirement for outdoor applications. This specification is acceptable for consumer electronics.

Uniformity

The uniformity of PDLC electro-optical performance within a module and from module to module is essential for creating a seamless appearance of the modular display. The target value of ±2% was established during earlier work at Magnascreen Corporation.

Stability

Despite that PDLC is a self-sealing medium, some long-term degradation of electro-optical performance along the periphery of modules was observed. Changes such as dye fading along the module edges, observed in earlier work, delineated the modular construction of the display, thus disturbing its seamless appearance.

1.3 PROGRAM DESCRIPTION

The 21-month program consisted of a joint development effort between Magnascreen Corporation and Peregrine Optifilm, Inc. The tasks included:

- Develop the specifications required to produce a direct view display with acceptable optical performance .

- Analyze the chemistry of commercially available polymers.

- Identify links between chemistry and PDLC performance.

- Synthesize customized polymers with characteristics most suitable for the specified application.

- Optimize the liquid crystal chemistry.

- Synthesize the most promising Polymer/LC/Dye formulations.

- Produce test samples and test bed for evaluating the PDLC optical performance.

- Develop the coating process and equipment for production of highly uniform PDLC films.

1.4 PROGRAM RESULTS AND CONCLUSIONS

The results and conclusions can be summarized as follows:
- Sixteen commercial polymers were screened for potential use in PDLC.

- Twenty-six customized polymers were synthesized for testing in PDLC samples.

- Fourteen liquid crystal mixtures were tested in dyed PDLC samples.

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- Links between polymer chemistry and PDLC performance were established with the exception of hysteresis.

- The three most promising formulae were optimized in matrix designed experiments.

- A PDLC demonstrator was built and used for performance evaluation.

- A PDLC coater was redesigned and upgraded.

- A low cost PDLC manufacturing process was developed and demonstrated.

- Despite some reduction, hysteresis remains high, preventing analog gray scale applications.

- Dye additions in PDLC materials substantially increase the "turn-off" time and hysteresis.

- New halogenated liquid crystals improve resistivity and durability of PDLC produced by solvent-induced phase separation.

1.5 FUTURE PROGRAM OBJECTIVES

The following future program objectives are aimed at resolving the remaining weaknesses of the PDLC medium and introducing the PDLC to the market:
- Develop an understanding of hysteresis phenomenon.
- Develop a zero hysteresis PDLC formulation.
- Establish a purification technique for high volume manufacture.
- Evaluate potential commercial and government markets and applications for the various PDLC formulations developed through this program.

2. PDLC TECHNOLOGIES

The trapping of liquid crystalline phases in polymer matrices has been a well-known art for over 20 years (see for example French patent No. 2,139,537 or U.S. patent No. 3,872,050). Only the cholesteric phase devices have achieved commercial success as thermochromic devices in novelty and thermometer applications. Nematic and twisted nematic phase materials have always suffered from poor environmental stability, contrast ratio or both. More recently, improved liquid crystals and polymer technology have allowed researchers to make improved nematic-polymer combinations with display application potential.

Various groups have now approached the "Dispersion" of liquid crystals into polymers in all of the common polymer preparation and crosslinking modes, (Doane[1]). A variety of display applications have now been demonstrated for these materials.

An assortment of chemistries have been proposed for the polymer portion of this material. The Liquid Crystal Institute has done a great deal of work with epoxy components. These are normally cured with a thiol compound. Raychem-Taliq developed a process originally based on water soluble polyvinyl alcohol with emulsified liquid crystal as an oil phase. More recently, they have introduced emulsion polymers. Other groups (General Motors, EM Industries) have introduced UV-curing monomers as the matrix phase. These are normally held between glass while being cured by exposure to ultraviolet radiation. Acrylic monomers appear to be the material of choice.

The approach favored by our group is the solvent-induced phase separation, "SIPS" process. The components of the PDLC (such as polymer, crosslinker, and liquid crystal) are dissolved in a solvent, the mixture is cast out onto a conductive film surface and the solvent is allowed to evaporate. During evaporation, the phases separate. A top film layer is laminated

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[1] J.W. Doane, Chap. 14, Liquid Crystal Applications and Uses, B. Bahadur, Ed., World Scientific, (1990).

onto the mixture, and the crosslinking takes place over a period of hours to days. This is the technique utilized throughout the effort reported in this report.

3. TECHNICAL APPROACH

The technical approach of this project was built around the polymer portion of the PDLC. Due to their specialized nature, new liquid crystal components for PDLC's are of limited availability[2]. The polymer matrix of the PDLC material is the component that allows the normal experimenter and manufacturer to have the broadest opportunity for control of the PDLC electro-optical performance.

The rationale used here can then be explained as:

1) There exists incomplete information relating chemical structure to electro-optic performance.

2) There exists a large body of information and experience on electro-optic performance of many PDLC systems.

3) Available materials are not characterized for all of the properties required and chemical structures are not precisely defined.

4) Therefore this program:
   a) selected materials that provide the best match to the desired electro-optical performance and fully characterize each.
   b) determined the chemical structure of the best candidate structures.
   c) formulated test mixtures to test theories of chemically active groups on performance.
   d) synthesized new materials that provided the candidate chemistry and characterized electro-optic performance.

---

[2] EM Industries, Inc. produces new types of liquid crystals that are designed to be compatible with active matrix-driven PDLC's. This will be reported in Section 7.

Figure 1 describes the process in a flow diagram. Essentially, it involved the making of PDLC samples with well-characterized polymers and additives. The electro-optic performance and other pertinent properties (see Appendices A & B) of the prepared samples were determined and compared to ultimate product specifications. This bank of knowledge then allowed the experimenter to build new polymers comprising the best components found in the screened materials. From that information, refined products, additives and liquid crystalline materials were combined into optimized mixtures. The rest of this report describes the methods and results of this work.

TECHNICAL APPROACH

PEREGRINE OPTIFILM INC
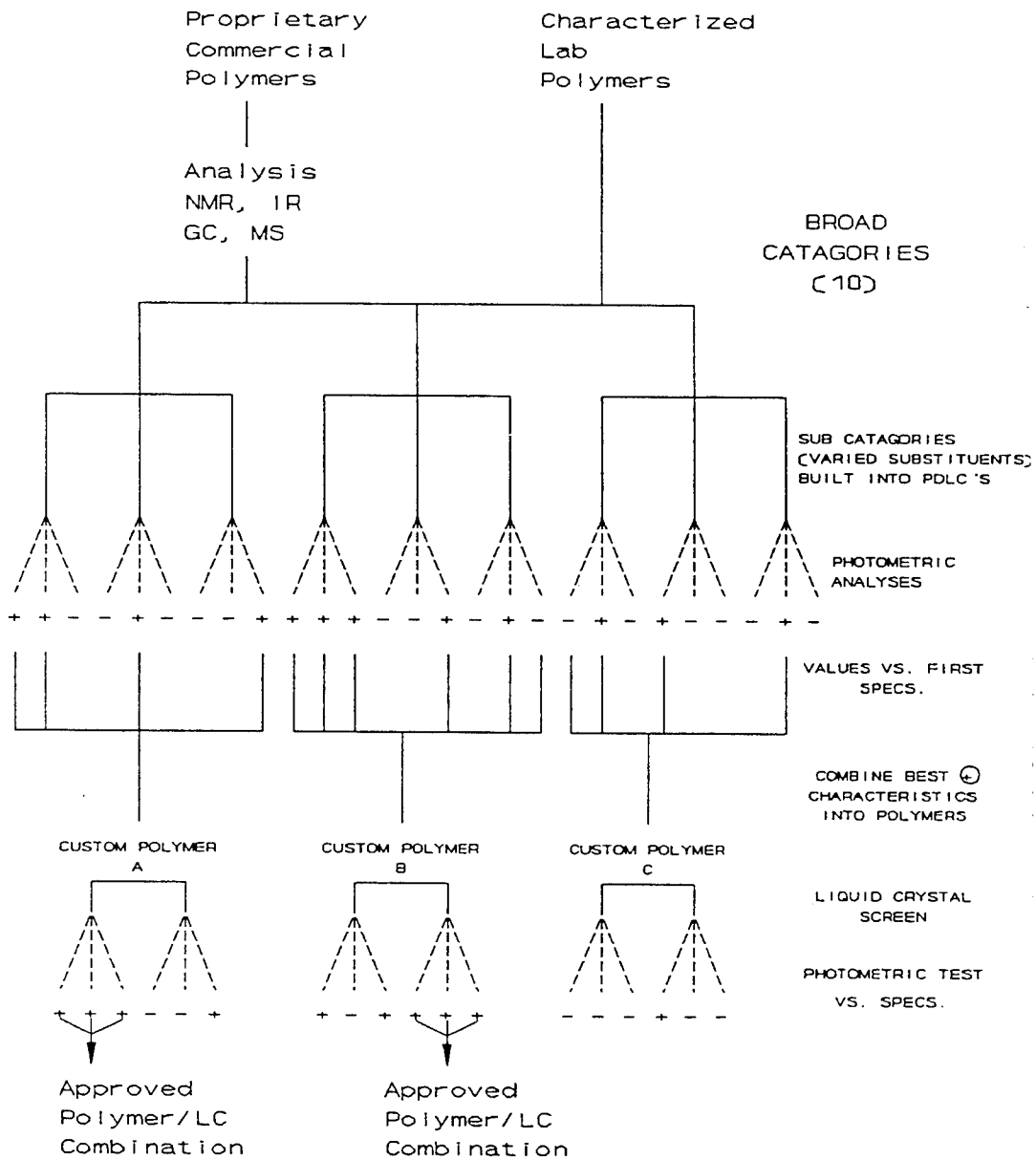
FIGURE 1.   Material development technical approach.

4. IDENTIFICATION OF COMMERCIAL COATING POLYMERS

The first step in developing an understanding of the polymer/liquid crystal relationships was to acquire a better knowledge of the commercially-available materials that had been found useful in earlier work. This included acrylic polymer products such as: AU 1033 from Rohm and Haas and SCX 800B from S.C. Johnson Wax. It was known that the products were primarily Poly Methyl Methacrylates (PMMA), but that they also contained other unknown components considered trade secrets by their manufacturers. In order to better understand the chemical makeup of those acrylic polymers, we required further analysis of an advanced nature.

Performing the simple analytical technique of infrared spectroscopy revealed little more than the PMMA structure. The samples needed to be hydrolyzed and the components separated and identified by the techniques of gas chromatography and mass spectroscopy (GC/MS) for a comprehensive analysis. The results are shown in Figure 2. Some important features of the polymers are, of course, the Methyl Methacrylate structure but also the nature and amount of the crosslinkable component. The AU 1033 contains a Hydroxy Propyl Acrylate and SCX 800B contains Hydroxy Ethyl Acrylate. The SCX 800B additionally contains a styrene component. Larger amounts of crosslink sites also relate to the enhanced "hardness" of the AU 1033 resin products. An epoxy component, EPON, which had been used in previous work was also analyzed and identified because it was felt that it might have use for this project.
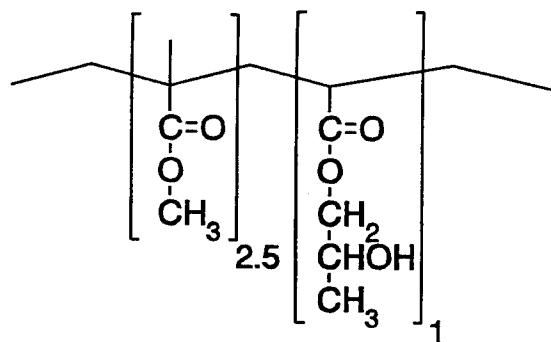
AU 1033
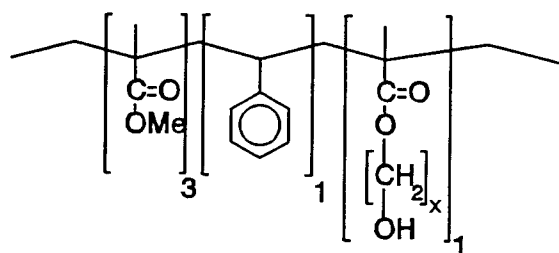
SCX 800B

An epoxy oligomer that we often used was found to be:
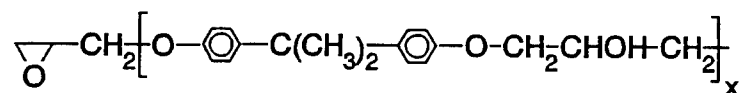
EPON

FIGURE 2.   Molecular structures for AU1033, SCX-800B & EPON.

Two other items, TA 43-6 and 671, were also included in the early analytical work. Those types of materials, however, turned out to be less useful during the PDLC screening phase. Further analyses were not done.

Certain research groups have also found that UV cured acrylic resins are useful for the formation of PDLC materials. Not many samples are available from these sources yet. Samples of those polymers that we have seen, so far, are simple mixtures of Hexyl Acrylic-type resins. This information that Hexyl Acrylics (a 6-carbon acrylic) and the PMMA's (1-carbon acrylics) make good PDLC matrices indicates to us that the in between acrylics (2-5 carbon acrylics) are likely to be good candidates for these applications as well. This information plus the results of our thermoplastic resin screening, as reported in Section 5, led us to concentrate our efforts in the area of Butyl Acrylics (4-carbon types).

5. RESULTS OF THERMOPLASTIC POLYMER SCREENING

There are a variety of thermoplastic acrylic and methacrylic polymers available from chemical supply houses such as: Aldrich Chemical Co., Milwaukee, WI. and Scientific Polymer Products, Inc., Ontario, N.Y. Of the available candidates, a certain number were not soluble in common solvent and, therefore, not usable with our PDLC system. We concentrated our efforts on producing materials from the Ethyl, Propyl, Butyl, Cyclohexyl, Phenyl, Norbornyl and Ethyl-Hexyl acrylics. These are 2-carbon through 8-carbon acrylics.

The polymers that contain the larger Ester groups (Hexyl through Octyl) tend to be quite soft, particularly because they are also not crosslinked. This softness seems to lead to weak walls in the matrix that separates the liquid crystalline zones of the PDLC, making them difficult to handle. Further work was concentrated on the less than 6-carbon type acrylics.

Previous experience had suggested to us that Methyl Acrylates (1-carbon) tend to produce small-droplet, high-voltage PDLC's. This information, coupled with the results of this early screening of thermoplastics (Tables 2, 3 and 4; see Appendix A for definitions of performance parameters), suggested to us that Butyl Acrylics (4-carbon) have the best opportunity for success. The Butyl-type samples represented some of the lower-drive voltage numbers and achieved the lowest hysteresis result. Being a "harder" polymer, it is also expected to form strong matrix walls in PDLC's. Additionally, it had been reported by the Liquid Crystal Institute that droplet alignment can be controlled to some degree. This is because Butyl Acrylate polymers tend to form radially-aligned droplets while Iso-Butyl acrylics tend to form axially-aligned droplets.

The number of favorable features of the Butyl Acrylic PDLC's was the basis for much of the work reported in the following sections of this report. The results obtained in the first phases of this effort indicate that improved acrylic polymers for PDLC will have certain characteristics:

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A.   It will consist mainly of 4-6 carbon Ester compounds (Butyl to Hexyl).

B.   It will contain some styrene.

C.   It will crosslink through a Hydroxy Ethyl Acrylate site. Previous work at Peregrine Optifilm has indicated that this could be an Isocyanate reactive group.

D.   It will contain the noncrosslinking to crosslinking component ratio of less than 1:4.

TABLE 2. Thermoplastic Polymers 1

Date	Compound	C/R	Tmin %	Tmax %	Von V	toff ms	Hy V
10/13/92	02 7:3 Butyl/i-butyl	8.30	11.56	95.7	47	16.5	1
11/30/92	02 T-Butyl/i-Butyl/800B	26.38	1.74	45.9	74.0	16.0	13
10/30/92	08 3:1 Butyl/iso	3.31	26.33	87.2	23	60.5	4
10/16/92	06 Methyl - TN0520	9.30	1.29	24.9	78	18.0	12
10/21/92	04R Ethyl	36.50	2.70	98.7	52	20.0	9
10/14/92	07 Hexyl	9.30	8.61	80.1	67	35.5	15
10/14/92	06 Cyclohexyl	14.00	4.67	65.3	61	60.0	12
10/14/92	02 Isobornyl	POOR FORMATION					

TABLE 3. Thermoplastic Polymers 2

Date	Compound	C/R	Tmin %	Tmax %	Von V	toff ms	Hy V
10/14/92	01 Benzyl	6.20	3.33	20.5	50	69.0	10
10/28/92	02 Phenyl	3.19	4.55	14.4	50	~	17
10/14/92	05 Butyl	51.50	1.50	77.3	69	11.0	8
10/14/92	12 Methyl	33.60	1.40	47.1	72	12.0	19
10/14/92	11 Ethyl	8.00	11.19	89.7	40	21.5	12
10/21/92	13R Butyl	4.21	23.73	100.0	40	15.0	12
10/14/92	15 2-Ethyl Hexyl	12.80	3.85	49.3	66	14.0	10
10/14/92	08 T-Butyl	31.70	1.61	50.7	75	10.5	18

TABLE 4. Thermoplastic Polymers 3

Date	Compound	C/R	Tmin %	Tmax %	Von V	toff ms	Hy V
10/15/92	01 Isopropyl Meth	10.0	4.0	40.5	70	3.0	10
11/02/92	10 Iso butyl meth	9.86	9.4	92.7	60	25.5	6
11/02/92	11 Butyl Meth	4.86	11.78	57.3	72	61.5	23
11/02/92	12 t-Butyl/Butyl Meth	8.84	4.84	42.8	75	47.0	16
11/02/92	13 Iso Butyl/Butyl Meth	6.69	8.94	59.8	73	36.0	15
11/04/92	01 Cyclohexyl Meth	5.54	7.37	40.8	72	104	9
11/04/92	02 Ethyl Acrylate	17.2	2.70	46.5	71	11.0	20
12/01/92	09 t-But/I-But/800B/1033	31.52	1.64	51.7	36.0	68.0	10

6. UNIQUE POLYMERS PREPARED FOR THE PROJECT

The new polymer phase of the program was divided into three parts:

    A.   Standard C,H,O Acrylics
    B.   Fluoro Analogs
    C.   Silyl Analogs

The "A" phase materials are based on resins manufactured by Dock Resins Corporation. These polymers are terpolymers or quadpolymers comprised of segments containing mixtures of some of the following:

Butyl Methacrylate	=	BMA
Isobutyl Methacrylate	=	IBMA
Methyl Methacrylate	=	MMA
Butyl Acrylate	=	BA
Isobutyl Acrylate	=	IBA
Hydroxy Ethyl Acrylate	=	2-HEA
Hydroxy Ethyl Methacrylate	=	HEM

A listing of the various combinations is compiled in Table 5. The preparation of fluorinated and silicon-containing polymers was also a goal of this project. Fluorinated compounds are generally of higher resistivity and stability than normal hydrocarbon polymers. A Japanese group (Hitachi) and EM, a German company, have also reported preparing UV-cured PDLC's that have potential as an active matrix-driven device while containing Fluoro Acrylic material. The refractive index of Fluoro Polymer can, however, be difficult to match to glass and polyester, so Silicon-Acrylics could potentially prove to be the best index-matching materials. The polymers in these classes are designated as "93-OXX" compounds and their structures are given in Figures 3 through 5.

TABLE 5.   Customized Polymers Based on DOCK Resins

TA 83-1	7 − BMA
	3 − IBMA
	1 − 2-HEA
TA 83-2	5 − BMA
	5 − IBMA
	1 − 2-HEA
TA 83-3	3 − BMA
	7 − IBMA
	1 − 2-HEA
TA 83-4	7 − BMA
	4 − IBMA
	3 − MMA
	2 − 2-HEA
TA 83-5	5 − BMA
	4 − IBMA
	3 − MMA
	2 − 2-HEA
TA 83-6	5 − BMA
	3 − IBMA
	1 − 2-HEA
TA 83-7	1 − BMA
	5 − IBMA
	1 − 2-HEA
TA 83-8	3 − IBMA
	5 − MMA
	1 − 2-HEA
TA 83-9	7 − BMA
	7 − IBMA
	2 − 2-HEA
TA 83-10	6 − BA
	2 − IBA
	1 − 2-HEM
TA 83-11	7 − 2-2EEA
	3 − IBMA
	1 − 2-HEA
TA 83-12	3 − BMA
	3 − IBMA
	3 − PMA
	1 − HEA

The prefix numbers, eg "7" in 7-BMA, indicate the proportion of
this monomer used in making the polymer.
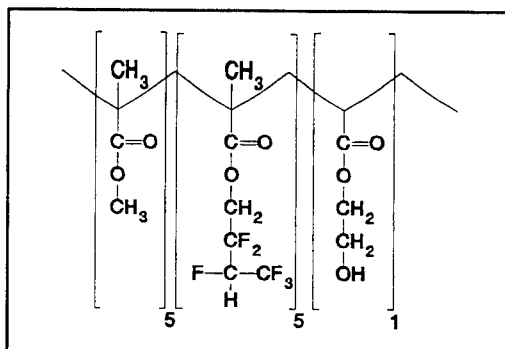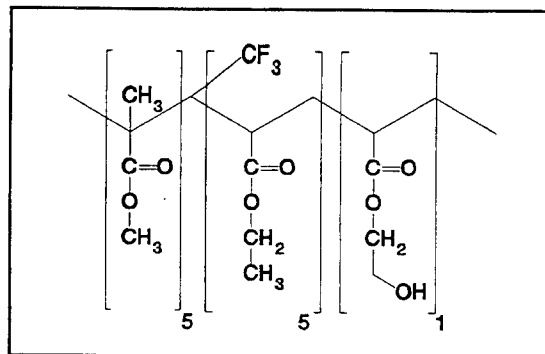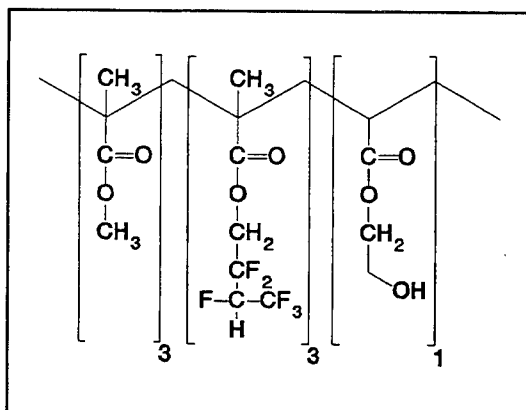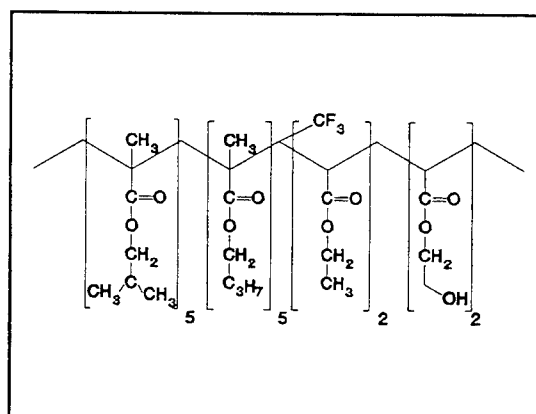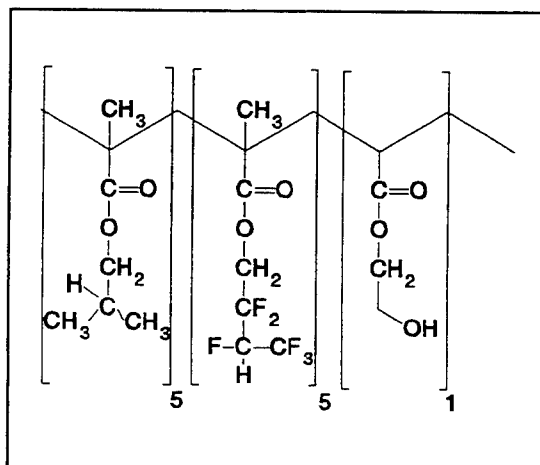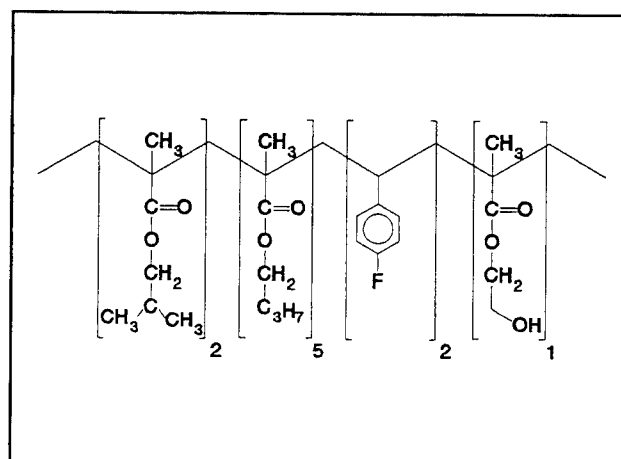
FIGURE 3. Fluoro analogs.

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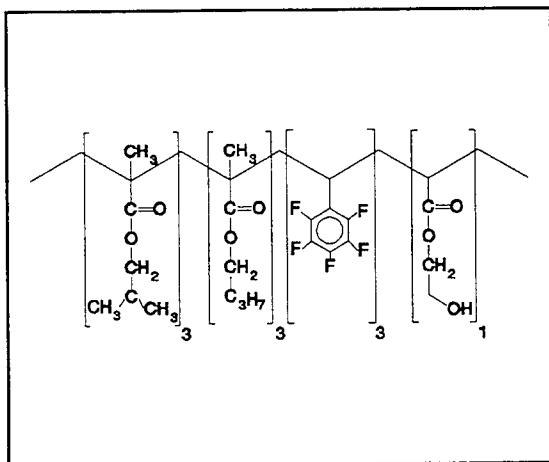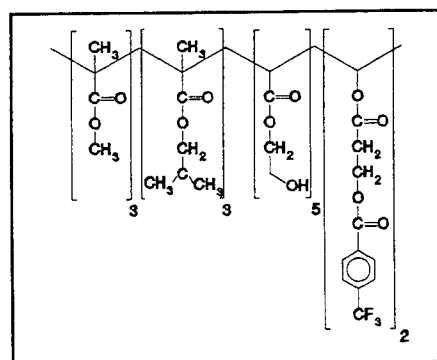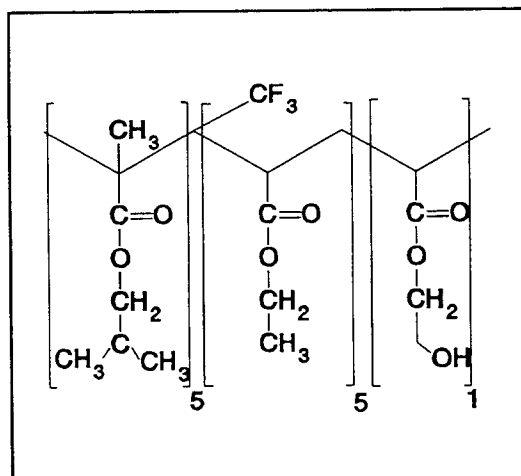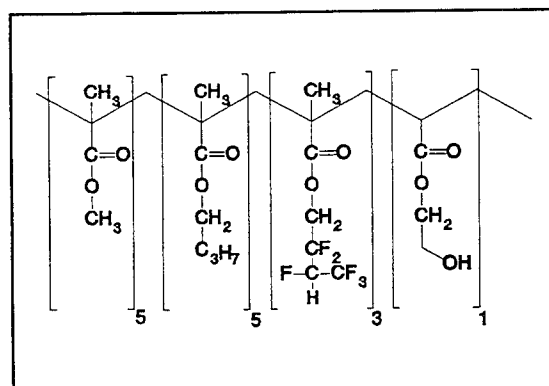
FIGURE 4. Fluoro analogs (Continued).

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FIGURE 5. Sylil analogs.
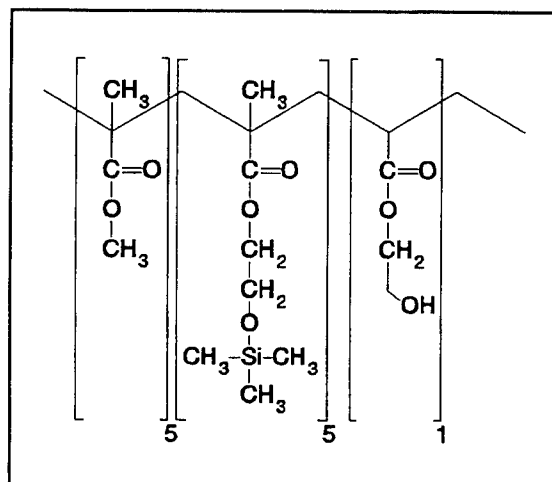
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93-021

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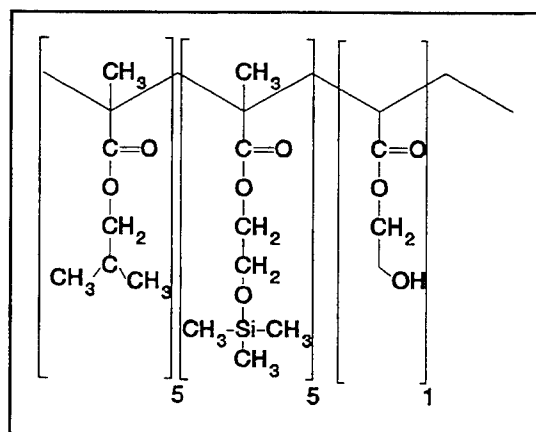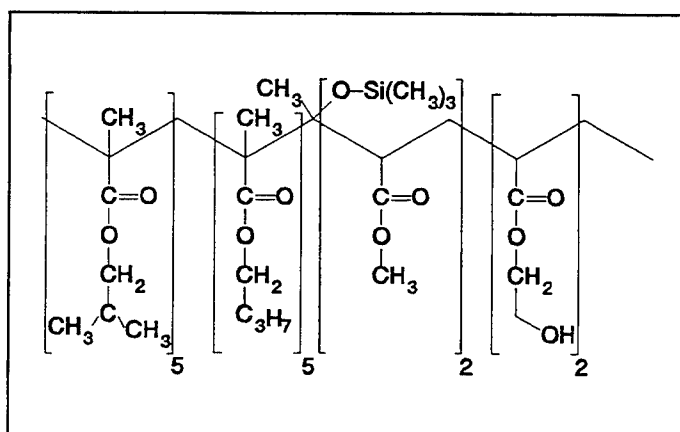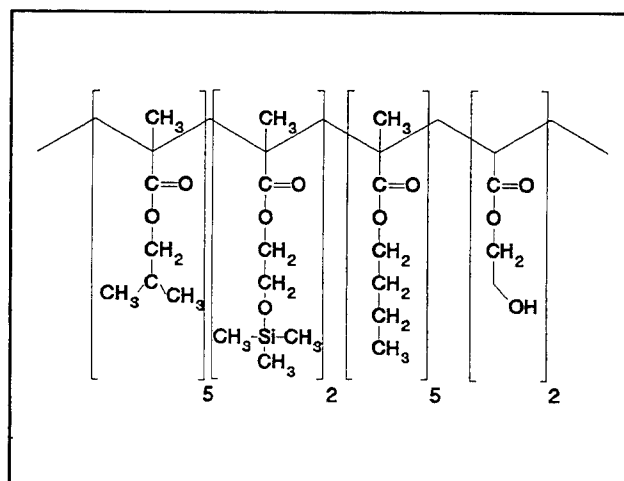
7. RESULTS OF LIQUID CRYSTAL SCREENING

7.1 CONVENTIONAL CHEMISTRY

The relationship of the liquid crystalline phase properties to
the PDLC behavior is a key issue in this science. The Peregrine
system lends itself well to an examination of a variety of liquid
crystal mixtures because its organic solvent component allows
PDLC's to be made from any conceivable liquid crystal. UV-curing
or epoxy-type PDLC's are limited to mixtures in which the liquid
crystal and monomer (oligomer) are mutually soluble. Table 6 is
a list of the most common liquid crystal mixtures used in the
screening phase of this project. Table 7 lists some of the
results of those experiments.

These data, combined with results of the polymer variation work,
indicate that the most important properties of LC mixtures are
dielectric anisotropy and optical anisotropy. The minimum
optical anisotropy values can be 0.16 in many of the good
samples. This is somewhat lower than the minimum number of 0.18
that is often considered the operative minimum in the industry.

In addition to the normal liquid crystal screening work, EM
Industries had been supplying samples of their new halogenated
liquid crystal materials and testing our mixtures for us. They
have had good success with these compounds (the TL series) in UV-
cured Acrylic systems designed for active matrix addressing (see
Appendix C). The strengths of the TL materials are their
excellent heat and UV durability, in addition, good optical
anisotropy of over 0.18. They do, however, exhibit low
dielectric anisotropy.

TABLE 6.   Liquid Crystals Properties

LIQUID CRYSTAL	N-I ($^\circ$C)	VISCOSITY 20°-22°C (cps)	$\Delta\epsilon$**	Δn (ri units)	n_o (ri units)	$V_{(10,0,20-22)}$ (volts)	$V_{(50,0,20-22)}$ (volts)
BL001*	61.0	39.0	13.80	0.2246	1.5216	1.50	2.05
BL033	69.0	40.0	17.40	0.2420	1.5290	1.48	2.02
BL036/BL015	95.0	67.0	23.10	0.2670	1.5270	1.76	2.38
BL046	83.0	52.0	13.20	0.2155	1.5201	1.69	2.29
E8*	71.0	54.0	15.60	0.2463	1.5249	2.10	1.44
E63	87.5	38.2	14.60	0.2240	1.5180	2.28	1.71
E70*	61-66	43.2	12.94	0.1870	1.5250	1.67	1.23
E80*	61-72	44.8	9.81	0.1630	1.5180	1.87	1.42
E170	60.0	43.9	5.22	0.1460	1.5075	2.67	2.01
E31LV	61.5	43.0	16.20	0.2270	1.5350	1.19	–
TN0403*	82.0	66.0	19.20	0.2580	1.5240	1.60	–
TN0510*	66.0	34.0	16.50	0.1990	1.5200	1.26	1.74
TN0621*	77.0	45.0	15.80	0.1940	1.5090	1.58	–
S605	97.5	44.0	13.20	0.1720	1.5000	1.80	–
S3028	72.0	21.0	7.30	0.1260	1.4950	2.07	–

* Used in "Best" samples
** Dielectric Anisotrophy

TABLE 7.   Liquid Crystal Screening

Date	Formula	C/R	Tmin %	Tmax %	Von V	toff ms	Hy V	Oven
12/21/92	01 BL009(108)	29.63	3.28	97.2	50	79.0	9	OK
12/21/92	02 E48(87)	22.39	4.44	99.4	36	41.0	4	Good
12/21/92	04 TN0605(80.4)	22.27	4.31	96.0	44	78.0	7	Good
12/21/92	05 TN0681(69.6)	27.49	3.51	96.5	32	48.0	5	Good
12/21/92	06 TN0601(101.6)	23.74	3.90	92.6	46	116.0	8	Good
12/21/92	07 TN4600(60)	14.77	5.98	88.3	71.0	34.0	5	OK
12/21/92	09 E41M(60)	1.53	5.93	9.1	77.0	2.0	3	Bad
12/21/92	11 E8(72)	32.27	2.95	95.2	27.0	68.0	4	Good
12/22/92	04 BL045(74) Low UV	14.81	6.38	94.5	29.0	139.0	6	Good +
12/22/92	05 E44(100)	14.11	5.77	81.5	71.0	21.0	11	Good +
12/22/92	06 BL042(79)	26.02	3.64	94.7	32.0	127.0	8	Good +
12/22/92	07 E63(87)	41.47	2.31	95.8	42.0	29.0	7	OK
12/22/92	08 BL041(89)	22.29	4.28	95.4	37.0	42.0	5	Good +
12/23/92	02 BL046(83)	42.92	2.33	100.0	27.0	72.0	7	Good +
12/23/92	03 E70(61)	32.85	3.02	99.2	17.0	101.0	7	Good +
12/23/92	04 E31LV(61.5)	46.99	2.09	98.2	19.0	100	9	Good +
12/23/92	05 E170( )	8.45	2.20	18.2	75.0	n/a	6	Good +
12/23/92	06 E180(67)	8.07	12.36	99.7	28.0	95.0	8	Good +
12/23/92	09 E208(87)	3.92	22.15	86.8	64.0	242.0	7	Good

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TABLE 8.   Liquid Crystal Screening (Continued)

Date	Formula	C/R	Tmin %	Tmax %	Von V	toff ms	Hy V	Oven
12/23/92	10 E204(90)	13.54	5.45	73.8	76.0	33.0	11	Good
12/23/92	11 Z4 4518(116)	4.38	17.06	74.7	74.0	56.0	16	OK
12/28/92	07 TN 430	8.90	10.86	96.7	20.0	105.0	6	Good +
01/11/93	02 BL003/83-1	6.72	14.12	94.9	27.0	73.0	8	Good
01/11/93	03 BL033/83-1	33.18	2.83	93.9	29.0	39.0	4	Good +
01/11/93	04 BL035/83-1	12.70	7.30	92.7	29.0	72.0	6	Good
01/11/93	05 BL046/83-1	55.00	1.74	95.7	31.0	57.0	6	Good +
01/11/93	08 BL035/83-1	23.01	4.02	92.5	40.0	64.0	8	Good +
01/11/93	09 BL046/83-1	66.79	1.40	93.5	36.0	38.0	7	Good ++
01/12/93	07 83-1/E80	31.74	3.11	98.7	19.0	71.0	5	Good +
01/12/93	13 S006/E7 +2%	33.45	2.75	92.0	53.0	12.0	1	Good ++
01/13/93	06 E80/83-1	25.06	3.89	97.5	16.0	120.0	7	Good
01/14/93	01 E80/83-1	25.29	3.95	99.9	16.0	81.0	7	Good +
01/25/93	09 E7/E201/83-2	25.05	3.92	98.2	10	49.5	6	Good
02/15/93	10 83-1/E70/E7+	39.71	2.45	97.3	20.0	39.0	4	Good
02/15/93	12 83-1/E48/0621	71.72	1.34	96.1	57.0	5.5	5	Good
02/17/93	06 83-1/E7+/BL009	23.38	4.23	98.9	26.0	38.0	4	Good
03/03/93	08 83-1/93002/E80/BL046	76.80	1.28	98.3	15.0	46.0	4	Good

7.2 NEW TL COMPOUNDS

The TL samples (202,212,205) were tested in various segments and
results are presented as white PDLC's in Figures 6 through 11.
These figures demonstrate the results in changes of liquid
crystal and liquid crystal concentration in a constant polymer
formula. These results yielded rather high drive voltage. We
believe that is due primarily to the low solubility of the new TL
compounds in the Acrylic matrix. Droplets form quickly in this
system and they are, therefore, quite small. Similar samples,
which are made from mixtures of TL and normal LC, have low drive
voltages as shown elsewhere in this report. The sample in Figure
6 exhibits a relatively low drive voltage. This material
contains a high proportion of silicone in the polymer matrix. We
believe that the driving voltage reduction is a result of larger
droplet size and, perhaps, a reduced surface energy differential
to overcome as the liquid crystals switch at the polymer-LC
interface.

(a)

sample: 083193-3 09-07-93 09:17

Trmax: 96.51 % 0.0 : 1 @ 99.3 V

Transmittance

100

50

0

0 6 12 18 Volts 30 36 42 48

—UP—
Tr 96.5%
10 7.0
50 10.0
90 17.0
Sp 0.43
Op 1.38

—DN—
Tr 96.5%
10 5.0
50 8.0
90 16.0
Sp 0.60
Op 1.39

Sw Sec
%149.18

Vh 2.0
FoM 6.3
ST 13.4
Sↄ 11.7

(b)

Tran=14.50 % (/div)
tswp=0.206 Sec points=412
Trace Menu Active 09-07-93 Time: 09:20
Frame # 5-1 ton 10.5 toff 18.0 31 V X Range [0.47 - 0.67]

Trans

1Sample 2SvSmpl 3DskOff 4XZoom 5Retrac 6List 7Title 8Cursor 9Param 10Exit

FIGURE 6. Electro-optic performance of PDLC containing 73% of liquid crystal TL 202 in standard polymer mix.
(a) Transmittance vs. driving voltage.
(b) Time response to a squarewave driving signal.

sample: 083093-1   09-13-93 13:09

Trmax: 90.51 %

100

T
r
a
n
s
m
i
t   50
t
a
n
c
e

0

0   6   12   18   Volts   30   36   42   48

-UP-
Tr 90.5%
10 16.0
50 27.0
90 41.0
Sp 0.69
Op 0.40

-DN-
Tr 90.5%
10 12.0
50 24.0
90 39.0
Sp 1.00
Op 0.44

Sw Sec
:149.17

Vh   3.0
FoM 17.1
S↑ .2.8
S↓   2.8

(a)

Tran=11.48 %   (/div)
tswp=0.147 Sec   points=295
Trace Menu Active   09-13-93 Time: 13:11
Frame # 53-1   ton 25.0 toff 10.0 41.3 V   X Range [0.33 - 0.47]

(b)

T
r
a
n
s

1Sample 2SvSmpl 3DskOff 4XZoom 5Retrac 6List 7Title 8Cursor 9Param 10Exit
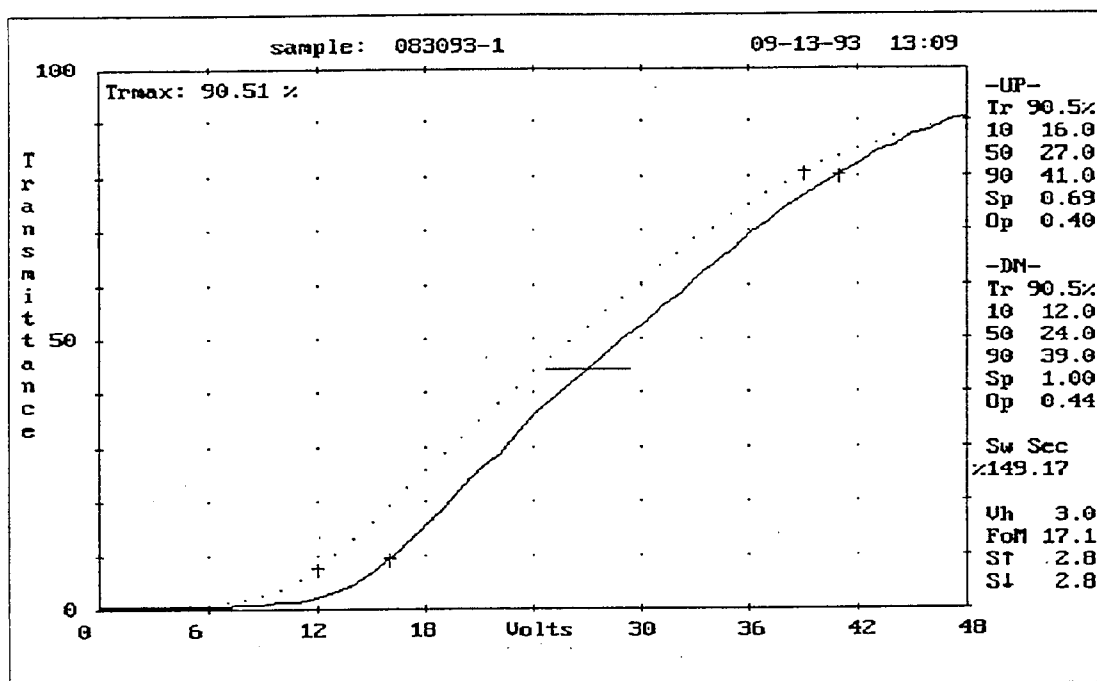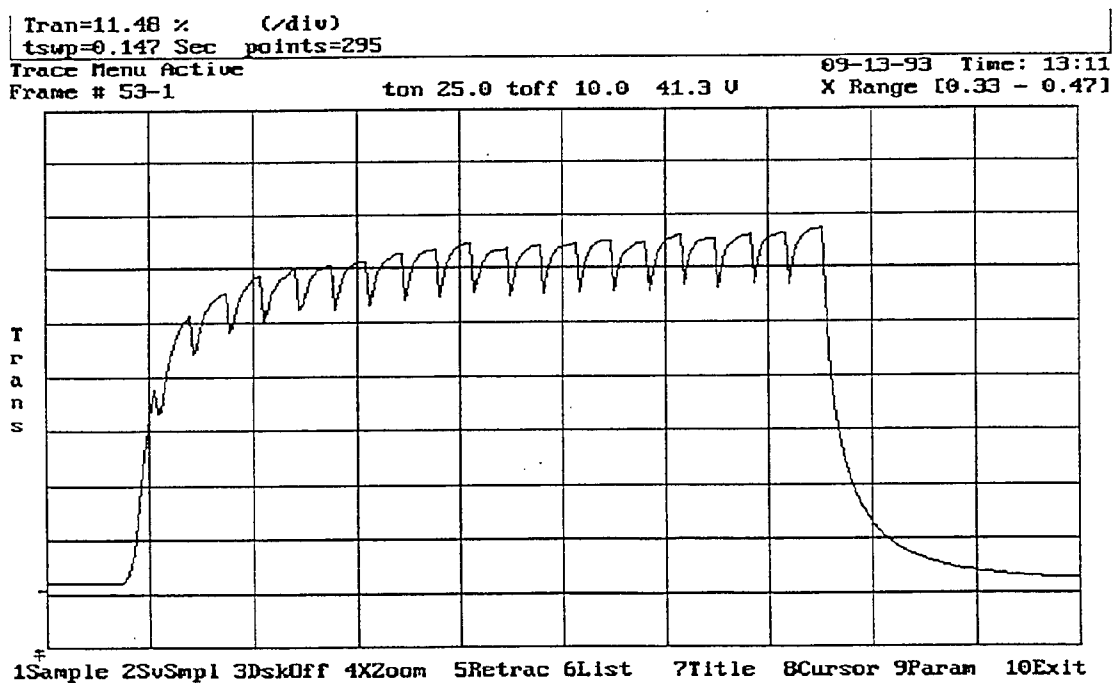
FIGURE 7. Electro-optic performance of PDLC containing 67% of
liquid crystal TL 212 in standard polymer mix.
(a) Transmittance vs. driving voltage.
(b) Time response to a squarewave driving signal.

31

(a)

sample: 083093-3   09-13-93 13:31
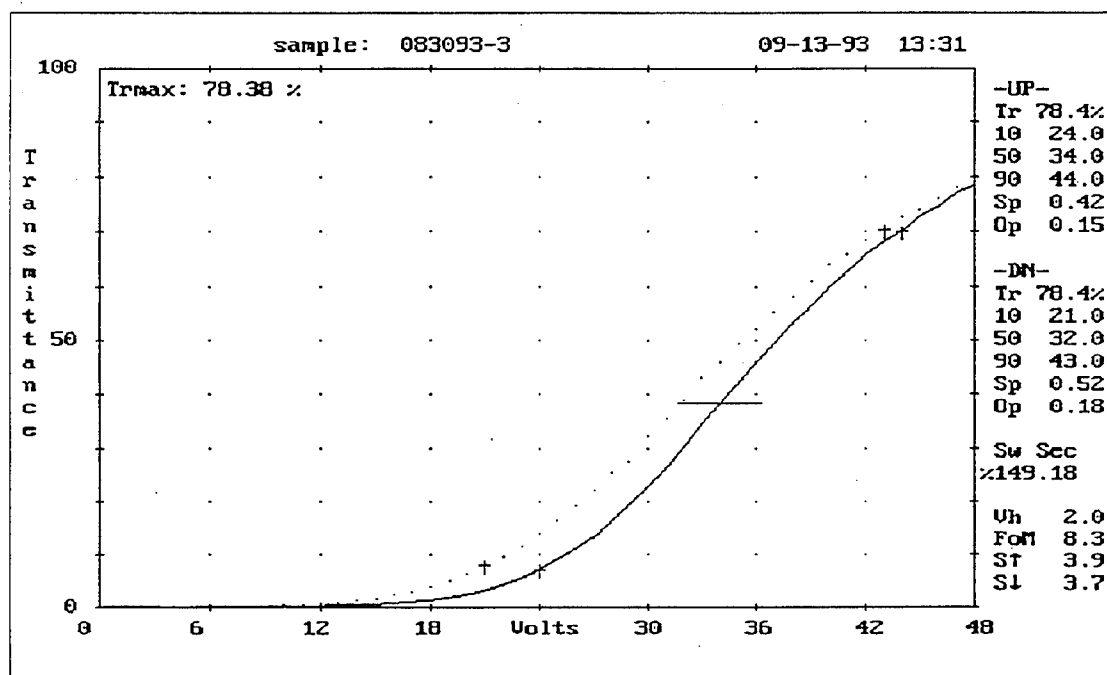
(b)
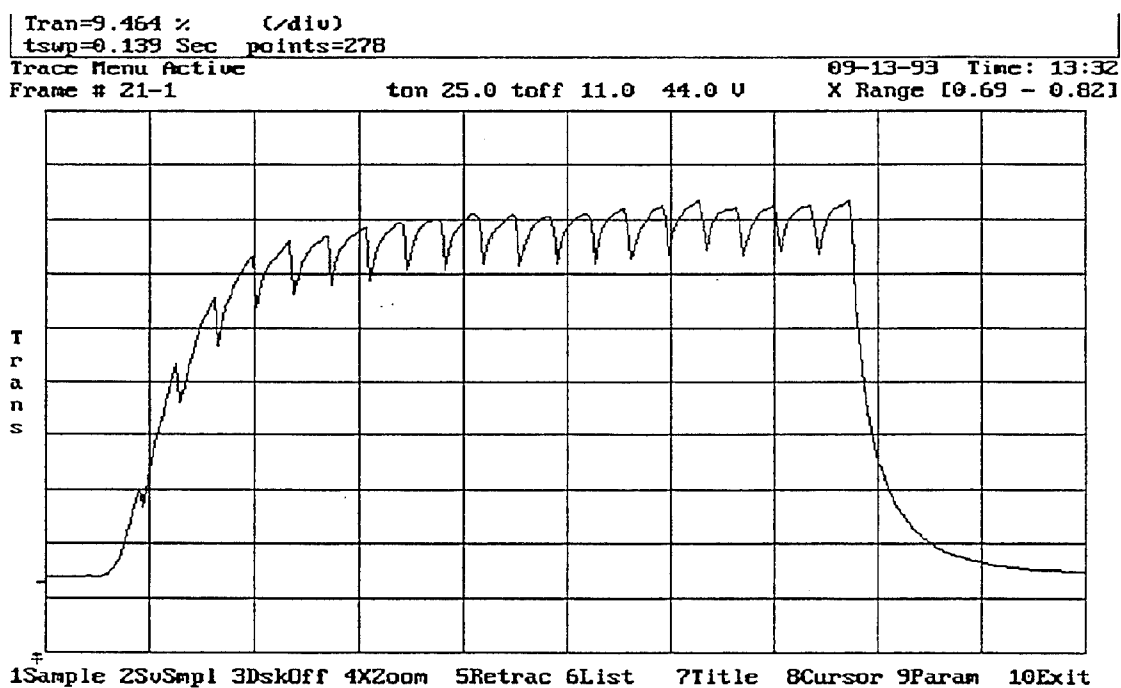
FIGURE 8. Electro-optic performance of PDLC containing 71% of liquid crystal TL 205 in standard polymer mix.
(a) Transmittance _vs_. driving voltage.
(b) Time response to a squarewave driving signal.

sample: 083093-4   09-13-93   13:44

(a)

100
Trmax: 89.48 %

Transmittance

50

0

0   6   12   18   Volts   30   36   42   48

-UP-
Tr 89.0%
10   9.0
50   15.0
90   31.0
Sp   0.67
Op   0.95

-DN-
Tr 89.5%
10   6.0
50   13.0
90   31.0
Sp   1.17
Op   1.14

Sw Sec
%149.18

Vh   2.0
FoM 18.7
S↑   5.4
S↓   4.3

Tran=11.48 %   (/div)
tswp=0.172 Sec   points=345
Trace Menu Active   09-13-93   Time: 13:44
Frame # 13-1   ton 10.5 toff 21.0   31.0 V   X Range [0.12 - 0.29]

(b)

Trans

1Sample 2SvSmpl 3DskOff 4XZoom 5Retrac 6List   7Title 8Cursor 9Param 10Exit
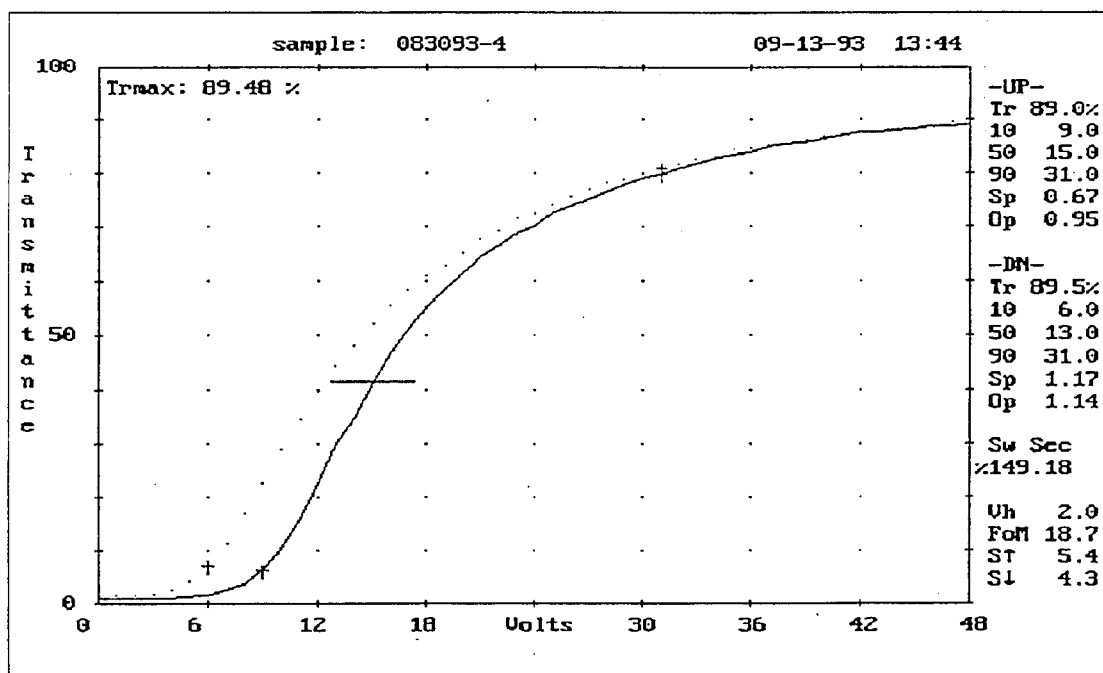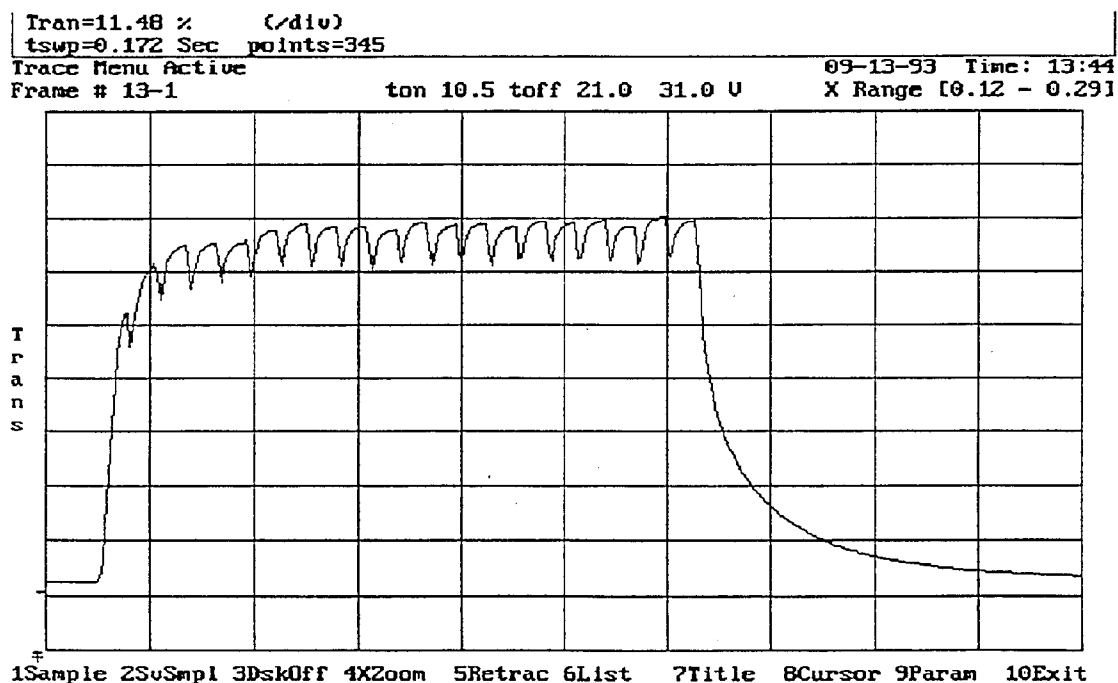
FIGURE 9. Electro-optic performance of PDLC containing 71% of
liquid crystal TL 212 in standard polymer mix.
(a) Transmittance vs. driving voltage.
(b) Time response to a squarewave driving signal.

33
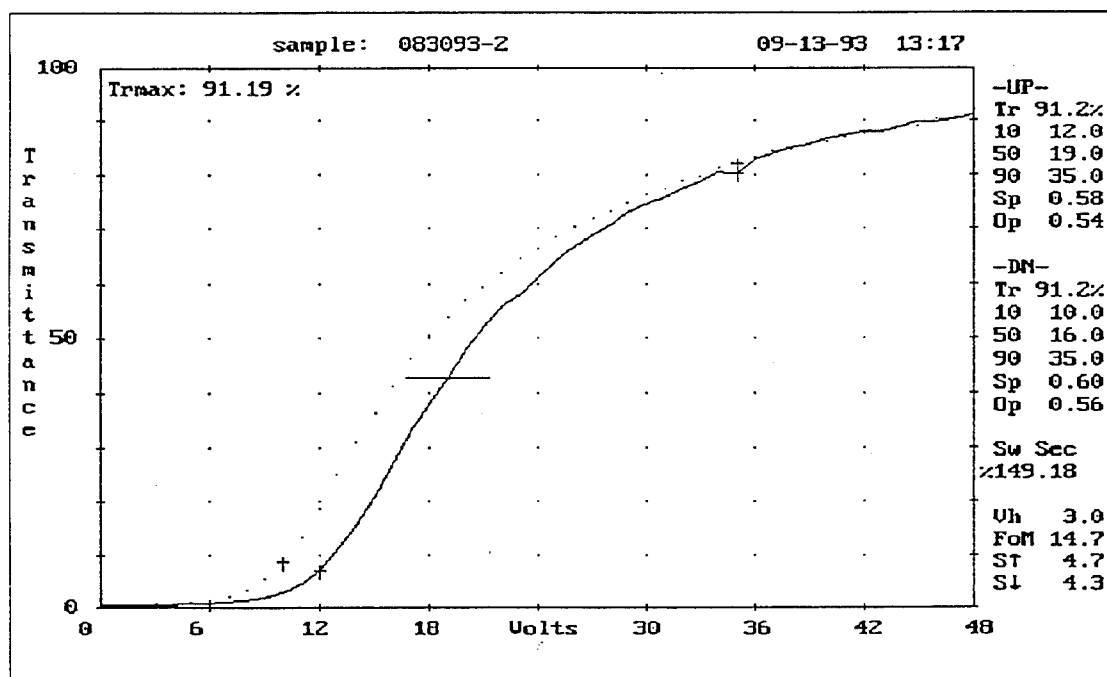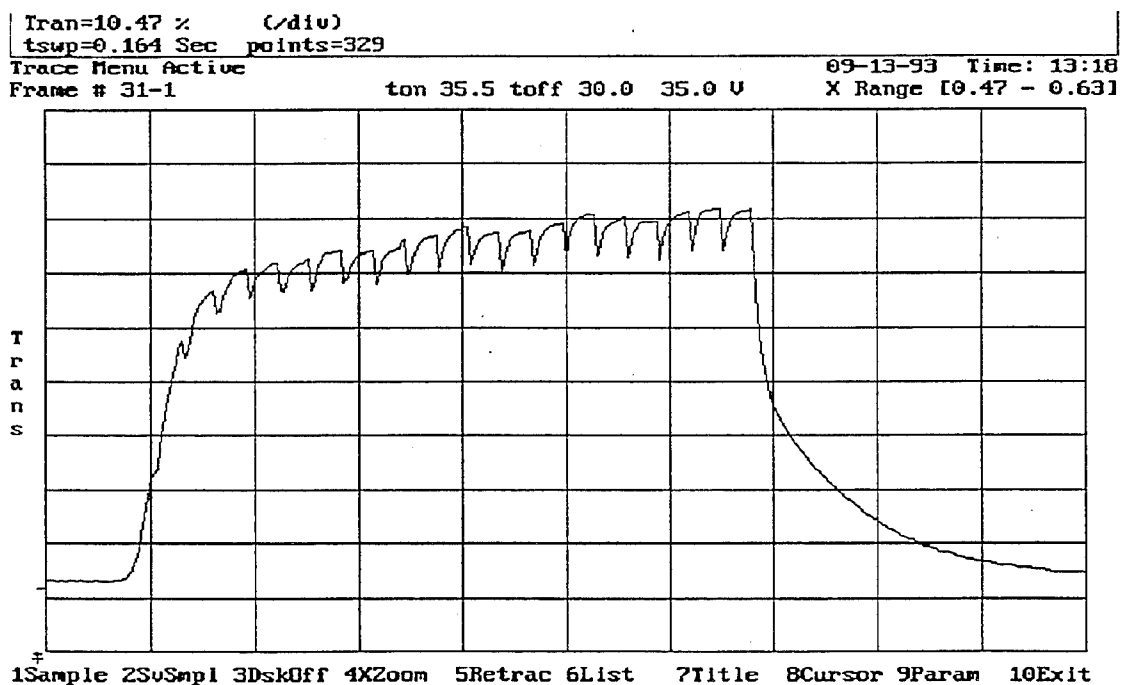
FIGURE 10.   Electro-optic performance of PDLC containing 71% of liquid crystal TL 202 in standard polymer mix. (a) Transmittance <u>vs</u>. driving voltage. (b) Time response to a squarewave driving signal.

(a)
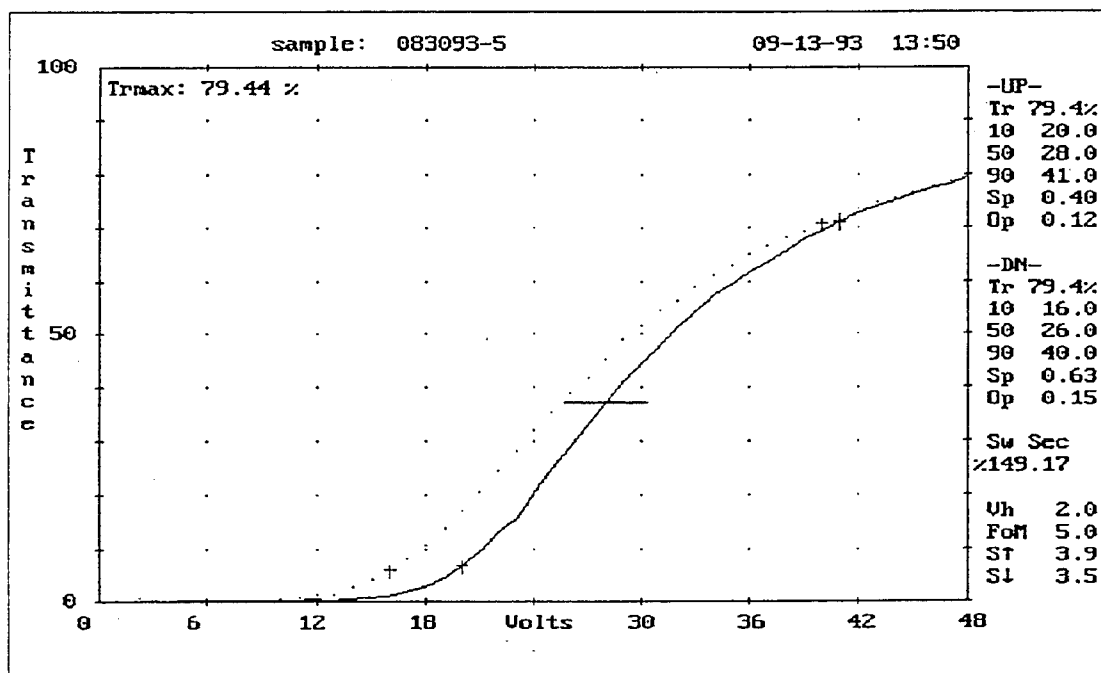
(b)
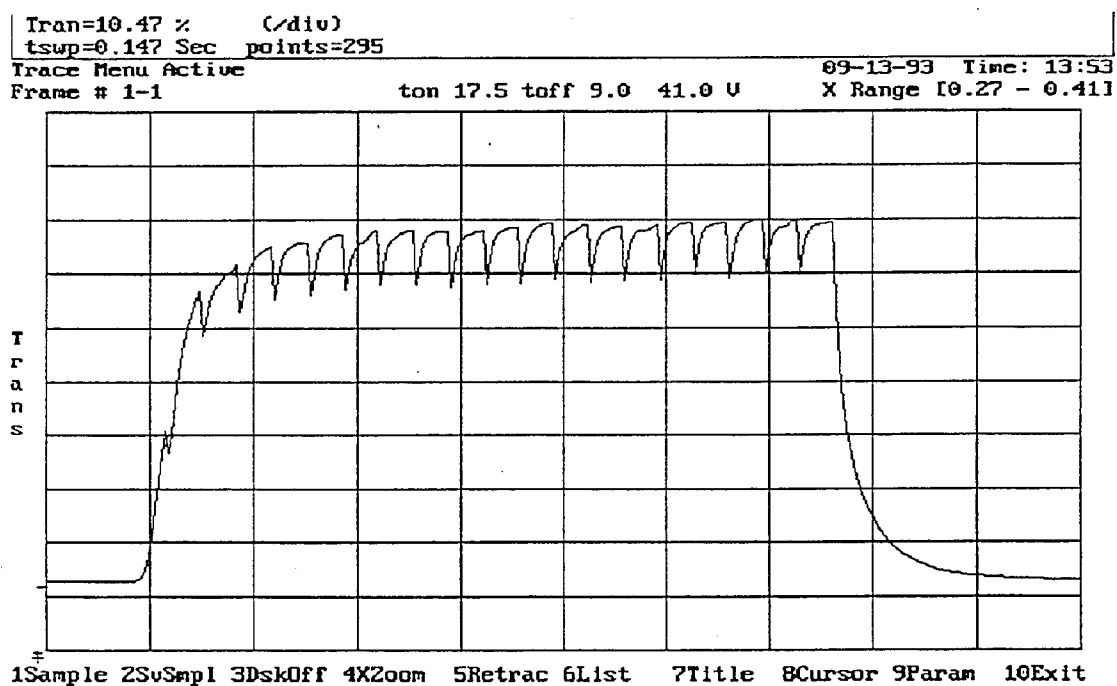
FIGURE 11.   Electro-optic performance of PDLC containing 75% of liquid crystal TL 212 in standard polymer mix. (a) Transmittance vs. driving voltage. (b) Time response to a squarewave driving signal.

8.   EFFECT OF VARIOUS FORMULA ADDITIVES

While the polymer and liquid crystal components are, of course, the most important ingredients in the PDLC, other chemicals can have a profound effect on performance. The crosslinker that stabilizes the polymer matrix is the most important of these.

8.1 CROSSLINKER CONCENTRATION

We commonly use a biuret crosslinker made from three molecules of Hexamethylene Diisocyanate that contains three active Isocyanate sites. In addition to this, we tested similar compounds, such as the Monomeric Hexamethylene Diisocyanate and its corresponding Isocyanurate Trimer. Neither the monomer nor the Isocyanurate yielded high-temperature durable PDLC's.

The crosslinker concentration also affects electro-optic performance. Figure 12 shows the T-V curves for a pair of similar formulae that differ in their crosslinker content. Sample 030493-8 contains a crosslinker content of 8% while sample 030493-9 contains 12%. The formula containing less crosslinker turns on at a substantially lower voltage, 35 V, rather than the 60 V of the second sample. This example is more extreme than some others, but this type of behavior is quite common.
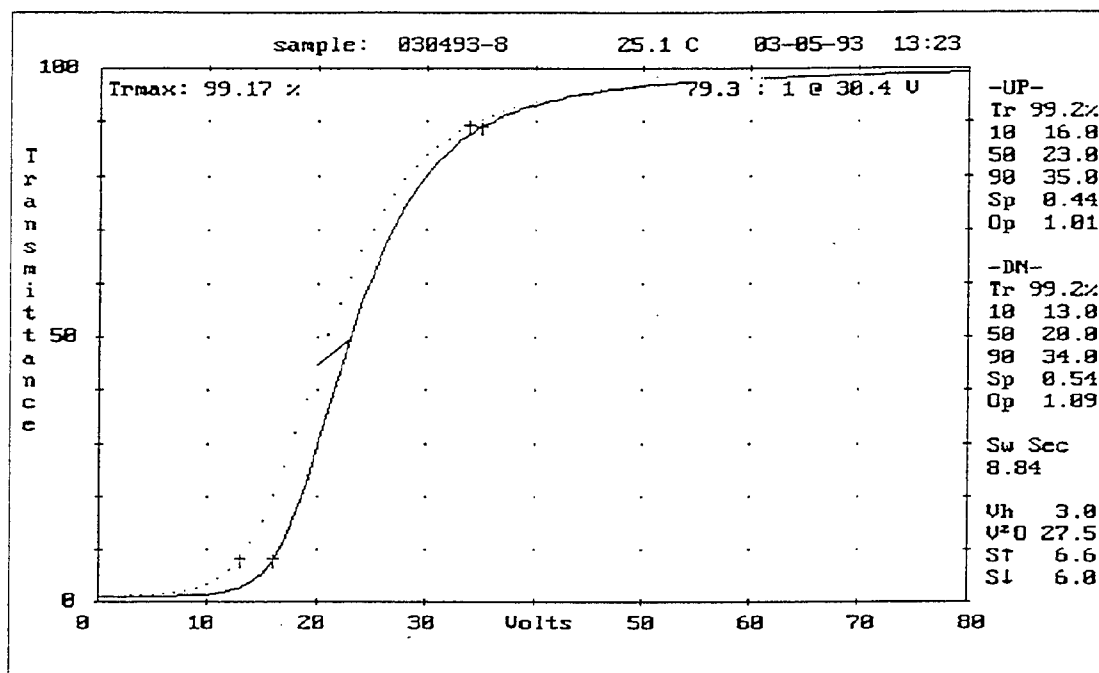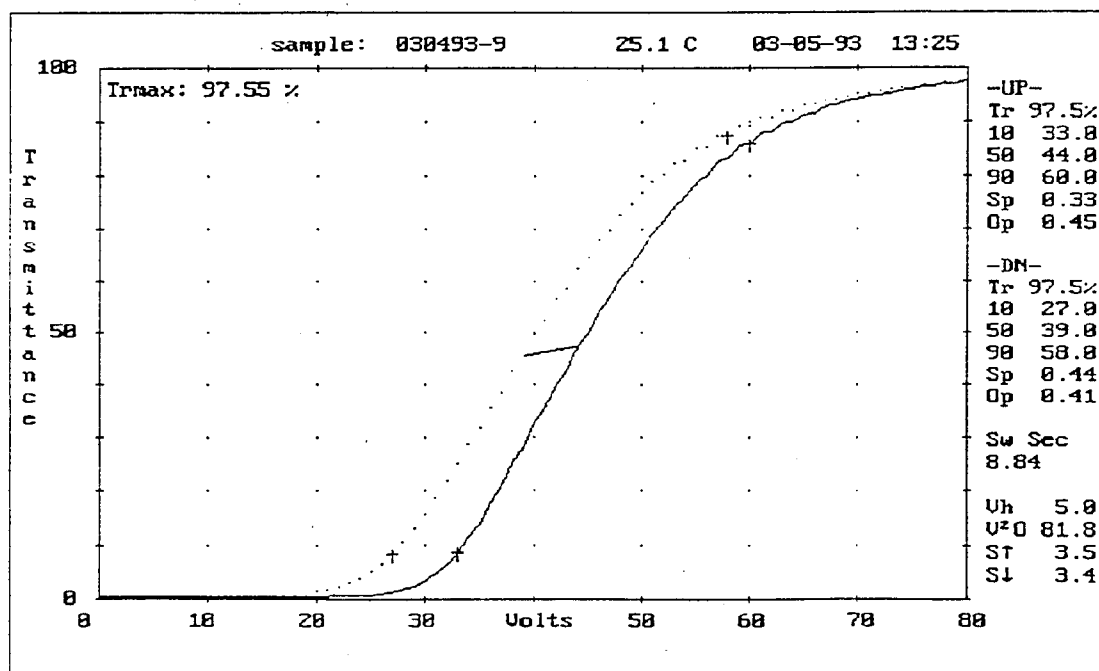
FIGURE 12. Effect of varying crosslinker concentration. Transmittance-voltage curves for PDLC containing;
(a) 8% of the crosslinker
(b) 12% of the crosslinker.

8.2 VISCOSITY MODIFIER

A number of additives were also introduced into the mixtures in
an attempt to reduce the viscosity of the liquid crystalline
phase. The compounds were chosen by the following criteria.
Each should be:

1. Liquid at room temperature but should have low vapor
    pressure.
2. Stable to heat and UV exposure.
3. 50% or more aromatic to dissolve well in the L.C.
    phase.

The three most useful compounds were found to be Fluoro
Naphthalene, Di PhenylEther and Phenyl ButylEther (Figure 13).
Figure 14 displays an improvement in the T-V curve of a PDLC that
contains 1-2% of Phenyl ButylEther (the bottom curve) as compared
with the same formula without the viscosity modifier. The effect
is more pronounced in PDLC's that have higher "on" voltages.
However, it is still important for the samples having drive
voltage of 20 V and less.
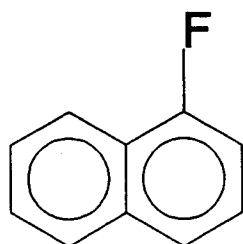
1 - Fluoronapthalene
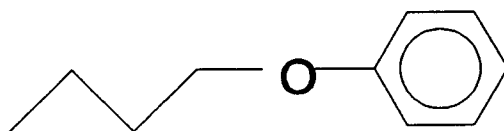
Butyl Phenyl Ether
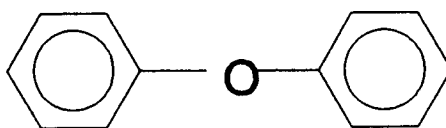
Di Phenyl Ether

FIGURE 13. Chemical structure of viscosity modifiers.

39
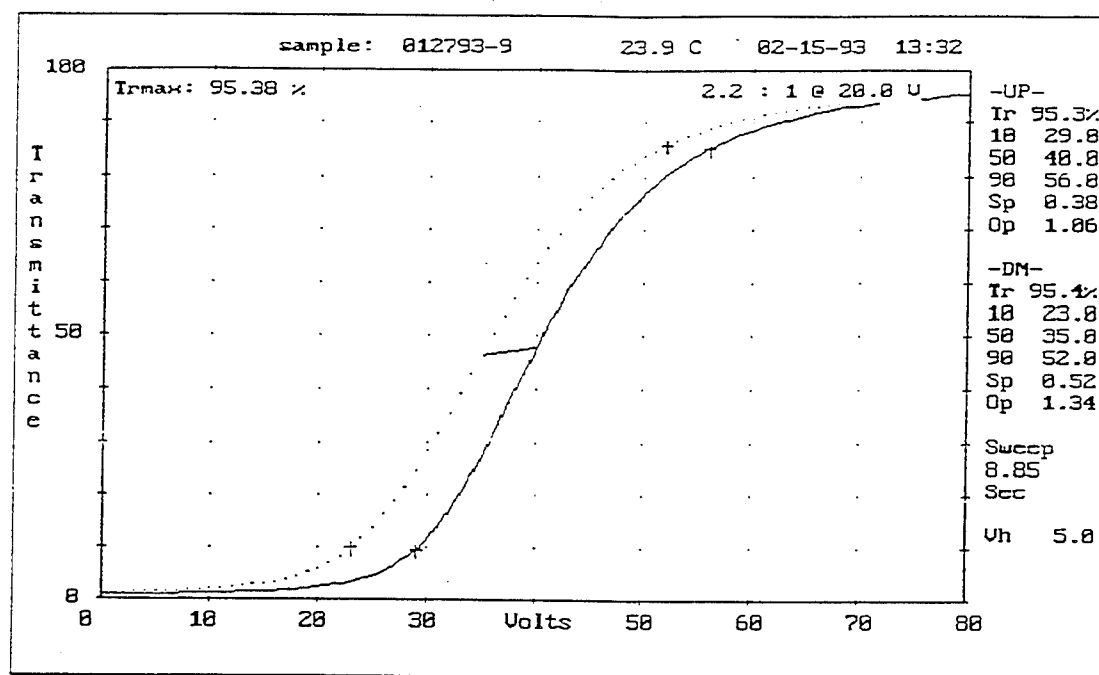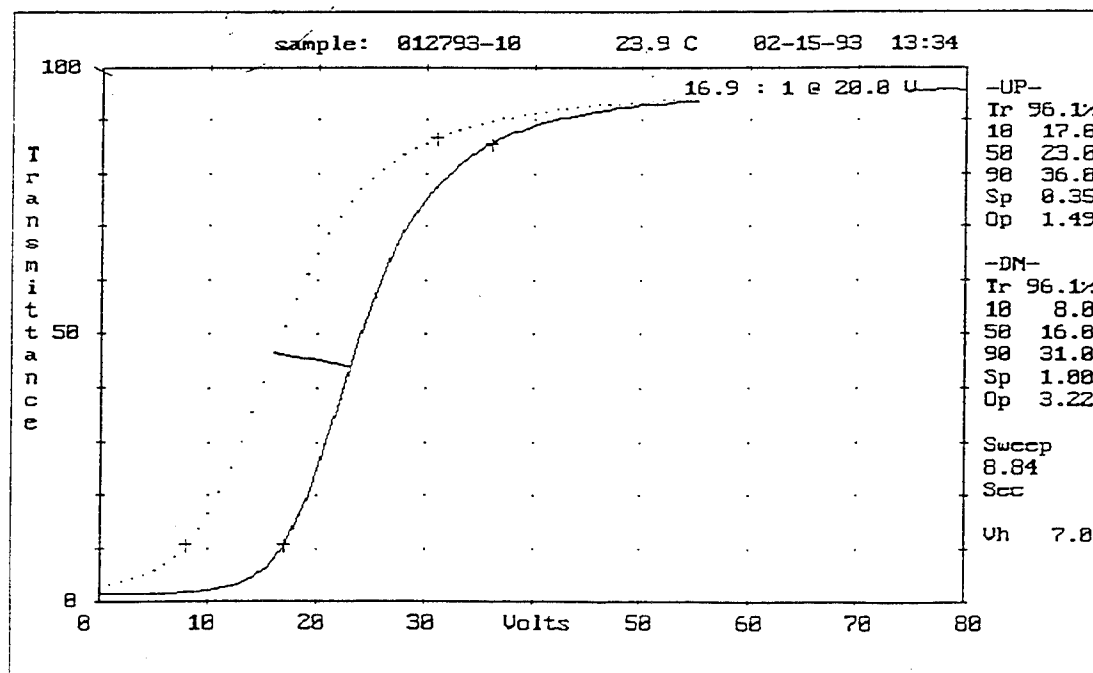
FIGURE 14. Effect of viscosity modifier on operating voltage; (a) no modifier (b) 2% of viscosity modifier.

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8.3   PARTICLES

A solid material in the form of milled silica particles was also
added to several PDLC samples.   Silica was chosen because its
refractive index is near that of the other components.   It is
expected that some of the solid will become part of the polymer
phase and the rest will become trapped in the L.C. phase, and
"breakup" some of the intermolecular liquid crystal attractions.
If that was true, the hysteresis of the system might be reduced.
Some evidence for hysteresis reduction was found (for examples,
see Figures 15, 16.   This type of formula would normally have 2 V
or more of hysteresis.   The two examples of the Figures, however,
have only one volt in these tests.   More on the hysteresis issue
will be addressed later in this report.

(a)


```
              sample:  101893-1              10-19-93  16:08
100
   Trmax: 78.13 %                    5.7 : 1 @ 99.3 U      -UP-
T                                                          Tr 78.1%
r                                                          10    8.0
a                                                          50   12.0
n                                                          90   21.0
s                                                          Sp  0.50
m                                                          Op 13.50
i
t                                                          -DN-
t  50                                                      Tr 78.1%
a                                                          10    6.0
n                                                          50   11.0
c                                                          90   20.0
e                                                          Sp  0.83
                                                           Op 13.46

                                                           Sw Sec
                                                           %168.01

                                                           Uh   1.0
                                                           FoM100.9
                                                           ST   7.8
  0                                                        S↓   6.2
    0      10      20      30    Uolts   50      60      70      80
```

(b)


```
 Tran=6.444 %        (/div)
 tswp=0.156 Sec  points=312
Trace Menu Active                          10-19-93  Time: 16:09
Frame # 27-1            ton 33.0 toff 31.0  59.7 U   X Range [0.43 - 0.58]
T
r
a
n
s
1Sample 2SuSmpl 3DskOff 4XZoom  5Retrac 6List   7Title  8Cursor 9Param  10Exit
```

FIGURE 15.   Effect of the addition of silica particles on PDLC
performance.
(a) Transmittance vs. driving voltage.
(b) Time response to a squarewave driving signal.

(a)

```
                    sample:  101893-2              10-19-93  16:02
  100
       Trmax: 73.09 %                      4.7 : 1 @ 99.3 V       -UP-
   T                                                              Tr 73.0%
   r                                                              10    5.0
   a                                                              50    9.0
   n                                                              90   19.0
   s                                                              Sp   0.80
   m                                                              Op  15.36
   i
   t                                                              -DN-
   t  50                                                          Tr 73.1%
   a                                                              10    4.0
   n                                                              50    8.0
   c                                                              90   18.0
   e                                                              Sp   1.00
                                                                  Op  15.38

                                                                  Sw Sec
                                                                  %168.02

                                                                  Vh   1.0
                                                                  FoM 90.9
                                                                  S↑   6.5
    0                                                             S↓   5.3
     0     10    20    30   Volts  50    60    70    80
```

(b)

```
  Tran=4.430 %      (/div)
  tswp=0.156 Sec   points=312
  Trace Menu Active                              10-19-93  Time: 16:03
  Frame # 13-1             ton 22.5 toff 66.5  19.3 V   X Range [0.30 - 0.46]
```



```
  1Sample 2SvSmpl 3DskOff 4XZoom  5Retrac 6List   7Title  8Cursor 9Param  10Exit
```
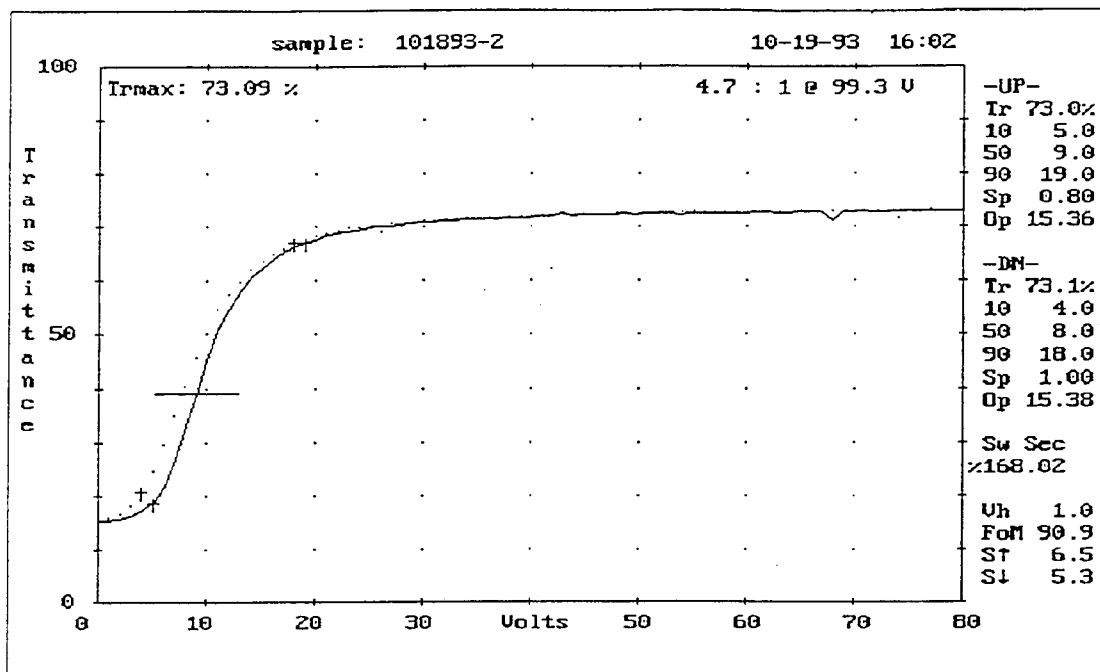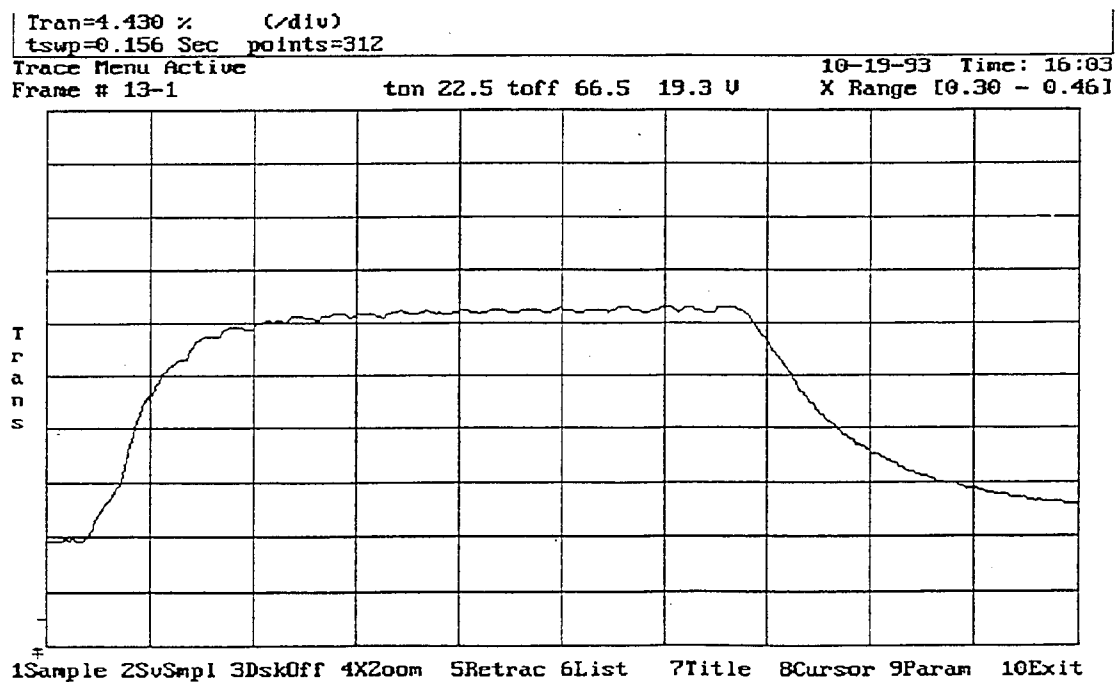
FIGURE 16.   Effect of the addition of silica particles on PDLC performance (continued).

(a) Transmittance vs. driving voltage.

(b) Time response to a squarewave driving signal.

9. EXPERIMENTAL DATA

This section contains the experimental results of a large number of tests which vary the formula parameters and compare the electro-optic data. Most of the information in this first part of Section 9 is from PDLC's which do not contain dye, but are used as the basis for the work reported in the latter part of this section.

Table 9 gives the results of polymer variation within an otherwise constant formula. This type of information is used to determine which type of polymer forms PDLC's with a good combination of C/R, V_{on} and t_{off}. From this data we found that the polymers 93-010 and 93-011 were preferred. Both polymers contain a trimethyl silyl fragment, so from these results we decided to use this type of chemistry in our dyed formulae.

Figure 17 presents the results of some of these samples in a different format. E Merck had offered to test a number of samples for us in their test equipment. The primary difference is in the "off transmittance" numbers and lower hysteresis. Their optical setup uses a slower sweep compared to ours and has a smaller collection angle. This underscores the importance of measurement conditions on the test results of PDLC characterization.

TABLE 9. Performance of PDLC with Various Polymers in an Otherwise Constant Formula

Polymer	Formula	C/R	Tmin %	Tmax %	Von V	toff ms	Hy V	Oven
92-005	120392-03	2	18.9	45	64	144	10	
92-007	120392-04	6	11.4	73	50	21	11	
83-1	120492-04	48	1.97	95	43	22	3	Good +
92-005	121092-09	11	7.93	86	36	39	4	Good
92-010	121692-01	31	2.70	83	27	29	3	Poor
92-011	121692-02	45	2.14	97	37	45	2	Fair
93-002/83-1	011193-10	44	2.15	95	19	47	5	Good
93-001/83-1	011293-03	67	1.09	73	42	20	5	OK
93-003	011293-05	96	1.02	98	50	12	7	Fair
93-006	011393-03	90	0.97	88	60	3	4	Good +
93-S006	011493-03	12	7.85	97	37	105	3	Good+
93-003	011493-09	59	0.94	56	69	16	8	Good+
83-2	011993-05	96	1.04	100	41	25	6	Good
83-3	011993-06	95	1.04	99	37	38	6	Good+
93-007	011993-07	48	2.06	99	20	99	4	Fair

Tables 10 through 12 give the results of a variety of tests
utilizing fluorinated and hydrocarbon acrylic polymers.
Fluorinated polymers tend to be high-resistivity, durable
materials. There have been literature reports of fluorine
containing polymers used for PDLC's that appeared to display low
hysteresis. Our results show a generally lower C/R and higher
drive voltage than the corresponding hydrocarbon acrylics. The
exception here is the last item on the list which contains a
fluorinated crotonate fragment, 93-018. We were able to achieve
a good contrast ratio simultaneously with low V_{on} and t_{off}. This
type of material was then incorporated into our matrix
experiments, which are reported in the next sections of this
summary.

The addition of black dye to these PDLC systems is required to
make a direct-view device with an acceptable contrast ratio.
First, a diffuser needs to be positioned between the liquid
crystal surface and the backlight source in order to simulate a
fluorescent back light. The measurement setup is shown in the
Appendix B.

A series of black dyed samples were then run in order to
determine the best concentration of dye for a given formula. The
base formulae were similar to those which had previously
displayed the best operational results. The electro-optic data
are shown in Table 13. The contrast ratios came out quite good
at over 20:1, however the black samples exhibit longer "off"
times.

TABLE 10. PDLC Performance for Various Polymer Mixtures Utilizing Hydrocarbon Acrylics

Polymer	Formula	C/R	Tmin %	Tmax %	Von V	toff ms	Hy V	Oven
93-009	12793-05	114	0.43	49	60	8	12	Fair
93-006	012893-06	58	1.71	99	17	41	6	Good +
83-4	021093-03	151	0.63	95	56	17	7	Good
83-5	021093-04	150	0.63	94	57	21	8	Good +
83-6	021093-05	78	1.21	99	32	26	3	Good +
83-7	021093-06	126	0.78	99	30	28	4	Good
93-010	021293-01	25	1.63	40	70	2	2	Good
93-011	021293-02	127	0.63	80	63	9	8	
93-012	021293-03	84	0.66	56	74	5	9	
83-8	021293-07				High			
83-9	021293-08	152	0.64	97	45	14	4	
93-010	021893-01	121	0.82	99	28	10	4	
93-011	021893-02	99	1.00	99	27	12	4	
93-012	021893-03	63	1.54	97	39	6	4	

TABLE 11. PDLC Performance for Various Polymer Mixtures Utilizing Fluorinated Acrylics

Polymer	Formula	C/R	Tmin %	Tmax %	Von V	toff ms	Hy V	Oven
83-7	021093-06	126	0.78	99	30	28	4	Good
93-010	021293-01	25	1.63	40	70	2	2	Good
93-011	021293-02	127	0.63	80	63	9	8	
93-012	021293-03	84	0.66	56	74	5	9	
83-8	021293-07				High			
83-9	021293-08	152	0.64	97	45	14	4	
93-010	021893-01	121	0.82	99	28	10	4	
93-011	021893-02	99	1.00	99	27	12	4	
93-012	021893-03	63	1.54	97	39	6	4	

Perigrine Optifilm PDLC
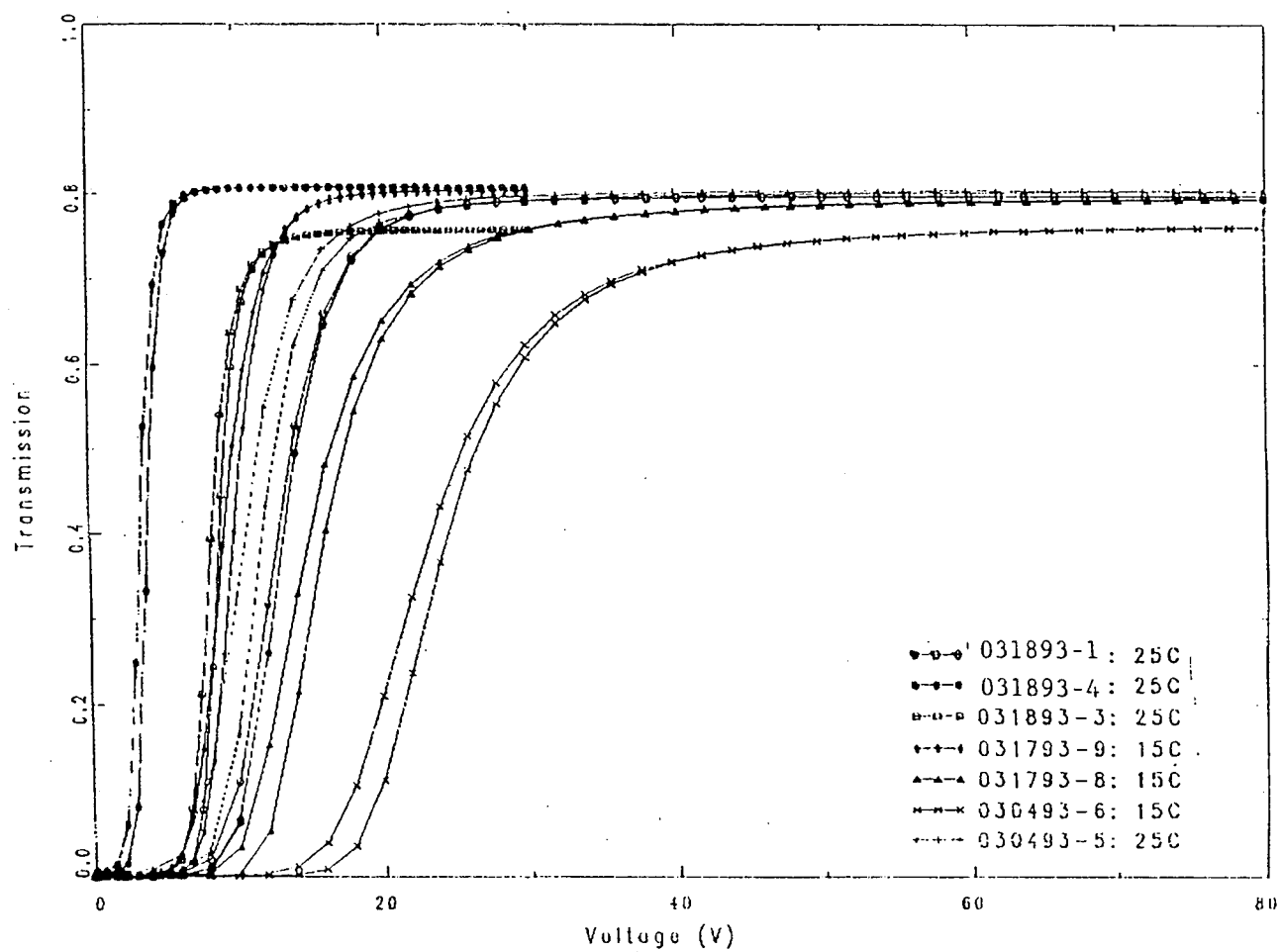
FIGURE 17. Low voltage samples tested by E.Merck Ltd.

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TABLE 12. The Effect of the Selected Polymers on Response Times and Operating Voltage

Date	Formula	Von V	ton ms	toff ms	Hy V	Oven	FoM
04/05/93	03 831/93027/570/02CN/5	13	39.0	56.0	5	Good ++	2.0
04/06/93	02 831/93027/510/PhOB/F	17	25.5	20.5	3	Good +	3.8
04/20/93	05 83-1/93-031/510/POB	13	71.0	47.0	5	Good	1.6
05/07/93	01 83-6/E7-510/FLNA	16	53.0	44.0	4	Good +	17.2
05/10/93	05 83-3/E70/E7+	21	35.0	47.0	4	Good +	2.5
05/18/93	01 83-1/E8/E70/FBIPH	11	20.0	60.0	4	Good +	1.5
05/27/93	03 831/8310/570/E70A/Sili	15	10.0	42.0	3		22.9
06/02/93	03 93-032/93-025/570/510	19	32.0	54.0	5		2.2

TABLE 13. Performance of PDLC Formulations Containing a Black Dye

Date	Formula	C/R	Tmin %	Tmax %	Von V	ton ms	toff ms	Hy V	Oven	FoM
04/27/93	05 83-1/93027/510/POB	10.02	4.04	40.5	13	36.0	175.0	6	Poor	10.2
04/28/93	05 83-1/93027/510/POB	23.44	1.51	35.4	39	9.0	120.0	6	Good	55.9
04/28/93	06 83-1/93027/510/POB	12.52	3.69	46.2	12	36.0	290.0	7	Good +	7.8
04/29/93	03 83-1/93027/E70-80/POB	14.60	1.98	28.9	14	55.0	110.0	5	Good +	5.9
04/30/93	03 83-1/93027/Silica	15.27	1.69	25.8	15	51.0	111.5	5	Good +	5.9
04/30/93	04 83-1/93027/Silica	11.85	2.75	32.6	14	40.5	105.0	5	Good	8.2
05/04/93	06 83-1/93022/027/E70-80	22.25	1.60	35.6	20	10.0	115.0	6	Good	10.7
05/05/93	01 83-1/93027/E70-80/Silic	3.03	12.76	38.7	12	1.5	long	4	Good	27.0
05/05/93	05 83-1/93022/027/E70-80	7.74	5.45	42.2	16	14.0	long	9	Good +	21.8
05/06/93	02 83-1/93022-027	18.40	2.50	44.2	19	11.0	160.0	9	Good +	14.5
05/06/93	09 83-1/93022/027/E48-70	28.17	1.80	50.7	45	12.0	33.0	6	Good +	104.4
05/07/93	02 83-6/E7-TN510/FLNA/	6.62	10.02	66.3	12	24.0	157.0	4	Good +	21.2
05/07/93	03 83-6/E7-TN403/FLNA/	14.61	4.56	66.6	14	17.0	110.0	6	Good	13.5
05/10/93	02 83-6/510/403/FLNA/SW	3.70	19.57	72.4	10	6.0	200.0	5	Good	28.0

10. POLYMER PURIFICATION AND CHARACTERIZATION

One of the goals in this project is to produce high resistivity PDLC materials of 10^{12} ohm cm or better. This is required to give the device a holding ratio of 95% in order to maintain high image quality as the display pixels are sequentially activated. Without that resistivity the image will fade and C/R will drop.

The polymers used in this work were all custom made in small amounts without special attention being paid to eliminate sources of contaminants. This was necessary because of the large number of materials involved and the high cost of purification. We did, however, perform some purification and characterization work to determine how elaborate the process would be. This involved the determination of the conditions required to run a Gel Permeation Chromatographic (GPC) technique on the materials. Included in this work was a determination of the molecular weight of some of the polymers. This method also served to act as a "yardstick" for judging the batch-to-batch reproduceability of the polymer, while contaminants are either "washed out" with the solvent phase or retained on the chromatography column. The construction of a method for performing this type of work was important in developing a method for doing this on a large scale. The conditions and results are summarized as follows:

Materials and Methods

Standards: A set of well-characterized polystyrene standards with low dispersion was supplied by Polymer Laboratories. A set of polymethyl methacrylate standards of somewhat lower quality was obtained through Polysciences. The properties of these materials were assumed to be as stated by their manufacturer and were not independently confirmed.

Gel Permeation Columns: The column set consisted of a Lichrogel PS-4 (250mm X 7.0mm; E.Merck Darmstadt), a Phenogel 10^3 Angstrom (300mm X 7.0mm; Phenomonex), and a Lichrogel PS-4000 (250mm X 7.0 mm) connected in series. The columns were connected in the order listed with the first column being connected to the injector system.

HPLC Conditions: The chromatographies were performed using UV grade THF pumped at 1.0 ml/min. Detection was done by measuring the absorption at 214 nm. All injections were of 50 μl volume. The column was maintained at a constant temperature of 400°C.

Sample Preparation: The samples were supplied in toluene at approximately 50% polymer concentration. Standards were pure liquids or solids. For samples and PMMA standards, solutions of approximately 0.1% were prepared in THF. For polystyrene standards, solutions of approximately 0.01% were prepared in THF.

Chromatographic Data: Detector response was digitized to 14 bits precision and recorded on magnetic media. The acquisition rate was 2 samples/sec.

TABLE 14. Molecular Weight Analysis

SAMPLE	Mp	Mw	Mn	Mz	Mw/Mn
82-3	60,400	60,952	23,874	115,281	2.55
93-09	164,761	139,999	56,756	247,746	2.47
93-16	158,840	163,655	71,973	326,010	2.27
93-21	170,929	156,597	55,685	383,858	2.812

Additional parts of the thresholded (apodized) chromatograms, the chromatograms displayed as normalized mass and normalized number plotted against molecular weight, and the cumulative weight and mass distributions for each sample are provided in the Appendix 4. While the technique will improve resistivity, it is expensive to perform on a large (0.1 - 1 kg) scale.

Liquid-liquid extraction was also investigated as a means to purify the polymers on a larger scale. A 100g polymer sample was extracted with water and then with heptane. This water extraction is done in order to reduce the ion content and the heptane wash was designed to reduce the low molecular weight polymer fractions.

ICP Analysis Results

1. Ten grams of sample 83-2 resin was heated at 95°C for one hour and mixed with 2 ml of deionized distilled water. The resulting mixture was stirred for 10 minutes, and then allowed to stand for two hours. The water solution was filtered off and analyzed for Na, K and Cl. A "blank" water sample was also analyzed. The results are shown in the Table below:

TABLE 15. ICP Analysis Results

ION	H_2O SOLUTION (PPM)	"BLANK" H_2O (PPM)
Sodium, Na	8.7	3.1
Potassium, K	1.2	<0.50
Chloride, Cl	6.9	3.2

As Table 15 shows, the concentrations of Na, K and Cl in the water solution are more than double, compared with the deionized water itself ("blank" water). This result indicates that the ion concentrations in the polymer sample can be reduced by washing with the deionized water.

2. The resin, after removal of the toluene, was continuously extracted with heptane for 3 hours by the Soxhlet extraction technique. GPC analysis of the remaining resin (Chemir 01) and original resin (Chemir 02) "as received" were carried out, and the results are shown in Table 16.

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TABLE 16. GPC Analysis Results

Sample	Inj.#	Mn	Mw	Mz	D
Chemir 01	1	22580	54449	155797	2.411
	2	22423	54220	156883	2.418
	3	22500	54400	157272	2.418
	Avg.	22501	54536	156651	2.416
	C.I.	195	299	1896	--
Chemir 02	1	23622	52877	140887	2.238
(original)	2	23008	52006	135857	2.260
	3	23020	52205	140863	2.267
	Avg.	23217	52363	139202	2.255
	C.I.	871	1132	7185	--

As Table 16 shows, the weight and Z average (Mw, Mz) of the sample Chemir 01 after heptane extraction, are higher than those corresponding numbers of the original sample, Chemir 02, by -4% and 12.4% respectively. The number average (Mn) of Chemir 01 s lower than that of Chemir 02 by -3%. The D value of Chemir 01 (D=Mw/Mn) is higher than that of Chemir 02 by -7%. These results indicate that the heptane extraction of the sample resin 83-2 reduced the low molecular weight fractions.

Two of the polymers, 83-1 and 83-13, were then purified by the water-heptane extraction technique and the resulting samples were sent to E. Merck Ltd. for resistivity measurement.

They reported the following:

83-1 $= 1 \times 10^{11}$ Ω.cm
83-13 $= 4 \times 10^{10}$ Ω.cm

High resistivity polymer is an essential component of high resistivity PDLC. The resistivity and voltage holding ratio (HR), defined in Appendix A, are tied together through laws of physics. It is more convenient to measure HR rather then resistivity when working with PDLC, which is unstable under DC conditions. With a refresh rate of 60 Hz, the resistivity target value of 10^{12} Ω.cm is equivalent to HR = 97.5%.

From the purified polymers, PDLC films were prepared and returned to E. Merck for holding ratio determination. They found these values:

SAMPLE	HR (20°C)
9-7-93-1	66%
9-7-93-2	95%
10-29-93-4	88%
11-05-93-4	86%

These numbers, though somewhat below the goal of the program (HR > 97.5%), are promising as they were obtained after a rather simple water/heptane extraction process. E. Merck chemists have expressed confidence that our polymers can be further purified to meet the 10^{12} Ω.cm standard. Time/money constraints have not yet allowed us to go further with these efforts.

11. DESIGNED EXPERIMENTS, MATRICES I & II

The designed experiment part of this project revolved around the
development of three matrices, each using differing amounts of
the preferred polymers, liquid crystals, and additives. The
first two matrices were built to optimize contrast ratio and
minimize drive voltage. The polymers included combinations of
the normal hydrocarbon types, as well as fluorinated or silicon-
containing types. The liquid crystal mixtures consisted of
standard cyano-biphenyl mixtures, and in the case of Matrix II, a
small amount of chiral-twist agent. Various amounts of viscosity
modifiers were added to reduce the drive voltage.

The matrix combinations are shown in Figure 18 and 19. Matrix I
is a 6 factor by two level design. There are 64 possible
combinations and it was sampled as a 11/32 replicate. The
sampled cells are indicated by an "X." Matrix II is a 7 factor
by two level design. There are 128 possible combinations. It
was sampled as a one-quarter replication as indicated by the
"X's."

			0.3g(83-1) 0.4g(93-028)				0.4g(83-1) 0.3g(93-028)			
			0.2g (E30) 0.8g (510)		0.8g (E30) 0.2g (510)		0.2g (E30) 0.8g (510)		0.8g (E30) 0.2g (510)	
			(CS) 0.08g	(CS) 0.10g	(CS) 0.08g	(CS) 0.10g	(CS) 0.08g	(CS) 0.10g	(CS) 0.08g	(CS) 0.10g
0.1g (93-021) 0.2g (93-034)	0.01g(FLNA) 0.02g(PhOPh)	Dye 0.12g	X			X				X
		Dye 0.08g		X			X	X		
	0.02g(FLNA) 0.01g(PhOPh)	Dye 0.12g			X			X		
		Dye 0.08g		X		X				X
0.2g (93-021) 0.1g (93-034)	0.01g(FLNA) 0.02g(PhOPh)	Dye 0.12g	X				X	X		
		Dye 0.08g			X			X		
	0.02g(FLNA) 0.01g(PhOPh)	Dye 0.12g		X		X			X	
		Dye 0.08g	X				X			X

FIGURE 18. Matrix I – ratios of the ingredients used in the first designed experiment.

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Figure 19 matrix (Matrix II):

				0.3g (83-1) 0.4g (93-14)								0.4g (83-1) 0.3g (93-14)							
				0.2g (E80) 0.8g (510) 0.1g(E7+)				0.8g (E80) 0.2g (510) 0.1g(E7+)				0.2g (E80) 0.8g (510) 0.1g(E7+)				0.8g (E80) 0.2g (510) 0.1g(E7+)			
				(CS) 0.08g		(CS) 0.10g		(CS) 0.08g		(CS) 0.10g		(CS) 0.08g		(CS) 0.10g		(CS) 0.08g		(CS) 0.10g	
				.02g	.04g	.02g	.04g	.02g	.04g	.02g	.04g	.02g	.04g	.02g	.04g	.02g	.04g	.02g	.04g
0.1g (93-021) 0.2g (93-015)	0.03g(PhOBu)	Dye 0.005g		X							X	X						X	
		Dye 0.008g			X					X		X							X
	0.02g(PhOBu)	Dye 0.005g				X			X					X	X				
		Dye 0.008g					X	X					X		X				
0.2g (93-021) 0.1g (93-015)	0.03g(PhOBu)	Dye 0.005g					X	X					X		X				
		Dye 0.008g				X			X					X	X				
	0.02g(PhOBu)	Dye 0.005g			X					X		X							X
		Dye 0.008g		X							X	X						X	

(Make 1-2%)

(Make 2 EloAc/1 CS) Silwet (Make 10%)

FIGURE 19. Matrix II – ratios of the ingredients used in the second designed experiment.

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The samples were prepared as shown on the matrix diagrams and the products were tested, aged, and tested again. The results are shown in Tables 18 and 19.

The results from Matrix I and Matrix II are quite similar. Contrast ratios are often over 10:1, drive voltages are commonly 15 V or less and the oven tests are generally good. The problem, however, is the long "off" time of virtually every sample. Because we did not establish why the dye has such a strong effect on slowing the liquid crystal relaxation time it was necessary to address this shortcoming in Matrix III by adding a chiral twist agent CB-15 (E.Merck), which is known to produce faster "turn-off" times in nematic PDLC materials. In addition, reduction of the dye percentage added to the LC was to be explored as well.

TABLE 17. Matrix I Data

Date	Formula	C/R	Tmin %	Tmax %	Von V	toff ms	ton ms	Hy V	Oven	FoM	Thickness microns
61093 01	1-1	9.7	5.6	54.8	10.0	142.0	15.0	2	Good	8.0	37.5
61093 02	1-2	6.8	7.7	51.7	11.0	>150.0	15.5	2	Good	13.4	37.5
61093 03	1-3	11.3	4.9	55.0	15.0	113.0	21.0	1	Good	16.9	37.5
61093 04	1-4	9.3	7.2	66.9	16.0	106.0	23.0	2	Good +	28.6	37.5
61493 01	1-5	7.4	8.9	65.5	9.0	>150.0	31.0	2	Good	10.1	35.0
61493 02	1-6	6.9	8.8	60.4	11.0	>150.0	14.0	3	Good	15.4	36.2
61493 03	1-7	7.7	7.0	54.0	10.0	>150.0	9.5	2	Good	10.0	37.5
61493 04	1-8	11.9	4.0	47.7	11.0	>150.0	18.0	2	Good	7.1	41.3
61493 05	1-9	11.1	5.5	60.8	16.0	105.0	31.0	2	Good	22.0	45.0
61493 06	1-10	10.1	5.5	55.7	16.0	100.0	32.0	2	Good	22.0	42.5
61493 07	1-11	8.8	6.7	68.7	18.0	95.0	35.0	2	Good	34.8	40.0
61493 08	1-12	19.1	2.3	44.2	12.0	>150.0	17.0	3	Good	4.9	42.5
61493 09	1-13	12.9	3.7	47.8	10.0	>150.0	10.0	3	Good	5.3	37.0
61493 10	1-14	13.7	3.1	43.0	13.0	>150.0	21.0	2	Good	7.9	42.5
61493 11	1-15	7.5	7.6	56.6	11.0	>150.0	14.0	2	Good	13.3	42.5
61493 12	1-16	11.2	5.1	57.1	12.0	>150.0	17.0	2	Good	10.8	43.8
61493 13	1-17	15.6	3.0	46.0	17.0	74.0	29.0	2	Good	13.5	45.0
61493 14	1-18	17.5	2.4	42.0	16.0	79.0	27.0	1	Good	9.6	42.5
61493 15	1-19	8.3	6.7	55.6	13.0	>150.0	20.0	2	Good	16.8	45.0
61493 16	1-20	14.6	2.7	38.9	12.0	>150.0	22.0	3	Good	5.6	50.0
61493 17	1-21	8.3	7.1	58.8	10.0	>150.0	11.0	3	Good	10.1	38.8

TABLE 18. Matrix II Data

Date	Formula	C/R	Tmin %	Tmax %	Von V	ton ms	toff ms	Hy V	Oven	FoM	Thickness microns
62393 01	1.0	3.8	19.5	75.0	14.0	13.5	>150.0	3.0	Good ++	58.0	37.5
62393 02	2.0	7.9	8.9	70.2	9.0	19.0	>150.0	4.0	Good ++	10.1	39.5
62393 03	3.0	7.9	9.6	75.9	10.0	10.0	>150.0	4.0	Good ++	13.7	41.3
62393 04	4.0	10.5	6.9	72.6	17.0	24.5	>150.0	2.0	Good ++	31.5	45.0
62393 05	5.0	17.3	3.5	60.5	17.0	18.5	>150.0	3.0	Good ++	16.2	42.5
62393 06	6.0	9.8	6.2	60.5	20.0	13.5	124.0	2.0	Good ++	41.0	42.5
62493 07	7.0	13.6	4.1	56.2	13.0	16.0	>150.0	3.0	Good ++	10.4	46.3
62493 08	8.0	10.7	5.1	54.4	12.0	15.5	>150.0	2.0	Good ++	10.7	45.0
62493 09	9.0	13.5	5.3	70.8	21.0	10.5	96.5	3.0	Good ++	39.3	45.2
62493 10	10.0	4.2	15.7	66.5	28.0	28.0	277.0	7.0	Poor	237.3	43.8
62493 11	11.0	10.6	6.6	69.8	19.0	8.0	78.5	3.0	Good ++	39.1	42.5
62493 12	12.0	9.0	8.0	71.6	10.0	10.5	>150.0	3.0	Good ++	11.4	45.0
62493 13	13.0	11.8	5.3	62.5	32.0	34.0	85.0	6.0	Poor	113.3	45.0
62493 14	14.0	15.8	3.8	59.9	13.0	13.0	>150.0	3.0	Good ++	9.6	42.5
62493 15	15.0	19.7	3.2	62.7	25.0	9.5	87.0	3.0	Good ++	36.3	41.3
62493 16	16.0	11.7	5.3	61.9	10.0	9.5	>150.0	4.0	Good ++	7.5	42.5
62493 17	17.0	10.4	6.9	71.9	22.0	17.5	>150.0	3.0	Good ++	57.7	46.8
62493 18	18.0	9.6	7.4	70.9	9.0	8.5	>150.0	3.0	Good ++	8.4	43.8
62493 19	19.0	12.1	5.9	71.4	26.0	14.0	64.5	2.0	Good ++	73.9	42.5
62493 20	20.0	8.4	8.6	71.8	14.0	16.5	>150.0	3.0	Good ++	25.4	42.5
62593 01	21.0	11.9	5.3	62.5	17.0	22.5	>150.0	2.0	Good ++	24.1	40.0
62593 02	22.0	3.6	16.4	59.3	11.0	8.5	>150.0	3.0	Good ++	28.7	45.0
62593 03	23.0	12.4	4.6	57.0	31.0	40.0	109.0	6.0	Poor	90.2	43.8
62593 04	24.0	7.7	7.0	54.0	10.0	16.5	>150.0	2.0	Good ++	10.0	47.5
62593 05	25.0	13.9	4.6	64.3	22.0	9.5	82.0	2.0	Good ++	38.6	45.0
62593 06	26.0	11.5	5.9	67.7	24.0	8.5	60.0	1.0	Good ++	60.7	45.0
62593 07	27.0	14.8	4.8	70.3	18.0	13.0	106.0	2.0	Good ++	24.9	42.5
62593 08	28.0	11.7	5.8	67.4	16.0	19.5	77.5	2.0	Good ++	23.1	45.0
62593 09	29.0	11.0	5.3	58.2	11.0	9.5	>150.0	3.0	Good ++	9.3	45.0
62593 10	30.0	12.1	4.7	56.6	11.0	11.0	>150.0	3.0	Good ++	8.2	47.5
62593 11	31.0	9.0	6.5	58.4	11.0	13.0	>150.0	3.0	Good ++	11.4	45.0
62593 12	32.0	16.3	3.6	58.2	13.0	10.0	>150.0	2.0	Good ++	9.0	42.5

12. DESIGNED EXPERIMENT MATRIX III

This section addresses the design and results of the third matrix experiment. The primary issue left unanswered after Matrix I and II was, "Can the off-time be reduced to an acceptable level without substantially increasing the drive voltage?" To answer the question we extensively reviewed the black sample data from our previous survey work, as well as, designed experiments. We found that using polymer mix containing fluoro-styrene (93-019) instead of mix containing fluorocrotonate (93-014 and 93-034) tend to produce samples with faster "turn-off" times. The downside of this approach was that we gave up the trifluor coronate moiety which we felt to be a key ingredient for eventual control of the hysteresis.

Matrix III consisted, again, of fluorine, silicon and hydrocarbon polymers. The ratios and LC combinations were changed and more chiral liquid crystal was added for reasons explained in Section 11. The actual structure of the matrix is shown in Figure 20. The results (Table 19) show that we were somewhat successful in reducing the turnoff time with minimal loss of contrast and maintaining drive voltage at less than 20 V. The best combined results area of the matrix is the area designated D-13 to D-15. The average values for these three samples are:

$$C/R \quad = \quad 9.9 : 1$$
$$T_{max} \quad = \quad 63.7 \text{ \%}$$
$$V_{on} \quad = \quad 18.7 \text{ V}$$
$$t_{off} \quad = \quad 51.2 \text{ msec}$$

The switching times still do not guarantee video rate, but they are substantially improved over the earlier work.

			0.2g(83-1) 0.1g(83-13)				0.1g(83-1) 0.2g(83-13)				
			0.4g (E7) 0.2g (510)		0.2g (E7) 0.4g (510)		0.4g (E7) 0.2g (510)		0.2g (E7) 0.4g (510)		All 0.55g
			(CS) 2175	(CS) 2600	(CS) 2175	(CS) 2600	(CS) 2175	(CS) 2600	(CS) 2175	(CS) 2600	
0.1g (83-1) 0.2g (018)	0.01g(FLNA) 0.01g(PhoBu)	FL430 0.01g	X			X		X	X		
		Silwet 0.01g		X	X		X				X (D 13)
	0.02g(FLNA) 0.01g(PhoBu)	FL430 0.01g		X	X		X				X (D 14)
		Silwet 0.01g	X			X			X	X	
0.2g (83-1) 0.1g (018)	0.01g(FLNA) 0.01g(PhoBu)	FL430 0.01g	X			X			X	X	
		Silwet 0.01g		X	X		X				X (D 15)
	0.02g(FLNA) 0.01g(PhoBu)	FL430 0.01g		X	X		X				X
		Silwet 0.01g	X			X		X	X		

FIGURE 20. Matrix III - ratios of the ingredients used in the third designed experiment.

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TABLE 19. Matrix III Data

Formula	C/R	Tmin %	Tmax %	Von V	toff ms	ton ms	Hy V	Oven	FoM
3-C1	7.0	8.6	60.5	22.0	64.0	19.5	2.0	GOOD	71.7
3-C2	7.5	7.5	56.6	18.0	86.0	33.5	2.0	GOOD	39.1
3-C3	9.8	5.5	53.8	29.0	42.0	57.0	2.0	GOOD	35.3
3-C4	6.4	8.6	55.4	18.0	93.5	9.0	1.0	GOOD	44.8
3-C5	7.9	6.8	54.0	21.0	96.5	18.0	1.0	GOOD	50.9
3-C6	7.0	8.8	61.8	16.0	100.0	13.0	1.0		
3-C7	8.3	6.4	53.0	21.0	63.5	23.0	1.0	GOOD	47.6
3-C8	7.5	7.1	53.4	19.0	69.0	16.0	2.0		42.1
3-C9	9.2	5.7	52.3	18.0	>150.0	33.5	3.0	GOOD	29.9
3-C10	7.1	6.8	48.5	12.0	>150.0	7.5	3.0	GOOD	14.4
3-C11	9.1	6.9	62.5	12.0	95.0	17.0	2.0	GOOD	14.6
3-C12	8.2	7.8	64.0	16.0	54.0	22.5	3.0	GOOD	31.3
3-C13	7.8	7.7	59.9	13.0	>150.0	15.0	2.0	GOOD	19.5
3-C14	10.9	5.3	57.6	20.0	55.5	34.0	2.0	GOOD	35.2
3-C15	6.2	8.8	54.7	11.0	>150.0	13.0	3.0		15.5
3-C16	6.1	9.1	55.7	10.0	>150.0	8.0	2.0	GOOD	13.0
3-D1	8.3	6.5	53.9	22.0	74.5	15.5	2.0	GOOD	54.0
3-D2	7.4	6.1	45.0	36.0	62.5	18.0	1.0		
3-D3	7.2	8.8	63.0	34.0	39.0	15.5	1.5		
3-D4	2.7	19.3	52.0	31.0	55.5	9.0	1.0		
3-D5	8.3	6.1	50.5	20.0	95.5	16.5	2.0	GOOD	40.7
3-D6	8.5	6.1	52.0	32.0	>150.0	18.0	1.5		
3-D7	9.8	5.0	49.0	27.0	40.0	54.0	2.0	GOOD	69.4
3-D8	10.5	4.7	49.3	24.0	73.5	33.0	1.0	GOOD	48.7
3-D9	5.9	9.3	54.8	14.0	132.5	15.0	3.0		27.7
3-D10	7.9	6.8	54.0	22.0	80.0	19.0	2.5		
3-D11	9.5	5.8	55.0	26.0	>150.0	20.5	3.5		
3-D12	8.7	6.5	56.9	11.0	>150.0	8.0	3.0		11.3
3-D13	8.8	7.1	62.8	22.0	41.0	28.0	2.0		59.2
3-D14	10.9	6.0	65.3	17.0	45.0	29.5	3.0	GOOD	27.5
3-D15	10.1	6.2	62.9	17.0	67.5	24.0	3.0	GOOD	28.5
3-D16	7.8	7.8	61.1	12.0	135.0	11.5	3.0	GOOD	16.6

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13. PERFORMANCE DEMONSTRATION

The PDLC samples of various formulations were carefully characterized for their performance characteristics, as described elsewhere in this report. In order to establish a link between the measured parameters and their visual impact on a human observer, a PDLC performance demonstration was included in this program.

The PDLC demonstration test bed for the demonstrator consisted of three main components: a fixture, driving electronics and software for a PC computer. The fixture holds four glass substrates (laminated with a PDLC layer) in a 2x2 array. Each substrate features a 9x9 array of directly driven pixels so that the viewing area comprises an array of 18x18 pixels. Preprogrammed patterns, stored in a PC in the form of a bit map, can be displayed as black and white images. Signals from a PC output LPT1 are converted by the driving electronics into a squarewave signal (60Hz) which is sent to the selected pixels. The amplitude of the driving signal is controlled by an external DC power supply.

Figure 21 shows a front view of a fixture populated with four substrates and driving electronics. Static patterns were used to evaluate the contrast ratio and operating voltage, while a set of sequentially displayed images facilitated the evaluation of response times.

Three test beds were built in order to demonstrate a PDLC formulae customized for direct view, projection and reflective displays.

The original plan called for building a demonstration device from the preferred formula(e) of this work. At that time, however, we were having difficulties making uniform samples using formula D-14 (Matrix III). We decided to build demonstrators with a more easily coated mix instead. (The coating problem was later resolved by better adjustments of the coater.)

The direct-view substrates were laminated with formula 110393-3 which performance parameters were similar to the better samples of Matrix III. The turn-off time was quite long, similar to the earlier matrix samples (Fig. 22).

The substrates for the projection mode were laminated with formula 091093-4 (Fig. 23). This contains a fluorinated acrylic polymer, as well as a mixture containing 50% of the new high resistivity "TL" liquid crystal discussed earlier in this report.

The substrates for the reflective display demonstration were laminated with a formula which is a combination of the other two mixtures. The first formula exhibiting higher contrast ratio and lower drive voltage characteristics was combined with the second formula exhibiting faster switching times. The simple 1:1 ratio of the two formulae was used. The electro-optic results are shown in Figure 24. The drive voltage is somewhat higher (30 V) but it was decided to allow that to occur in order to vie for the faster switching times.

The results of the visual evaluation can be summarized as follows:

1. The achieved contrast ratio for direct-view (8:1) and reflective displays (5:1) was satisfactory when displaying large patterns, but marginal for smaller alphanumeric characters. The switching speed was too slow for good video. The operating voltage was somewhat higher than one would expect from Figures 22 & 24.

2. The projection mode demonstrated acceptable contrast ratio, low operating voltage (15 V) and fast switching times. As these observations are supported by electro-optic measurements, we believe that the formulation 091093-4 has an excellent potential for active matrix projection displays.
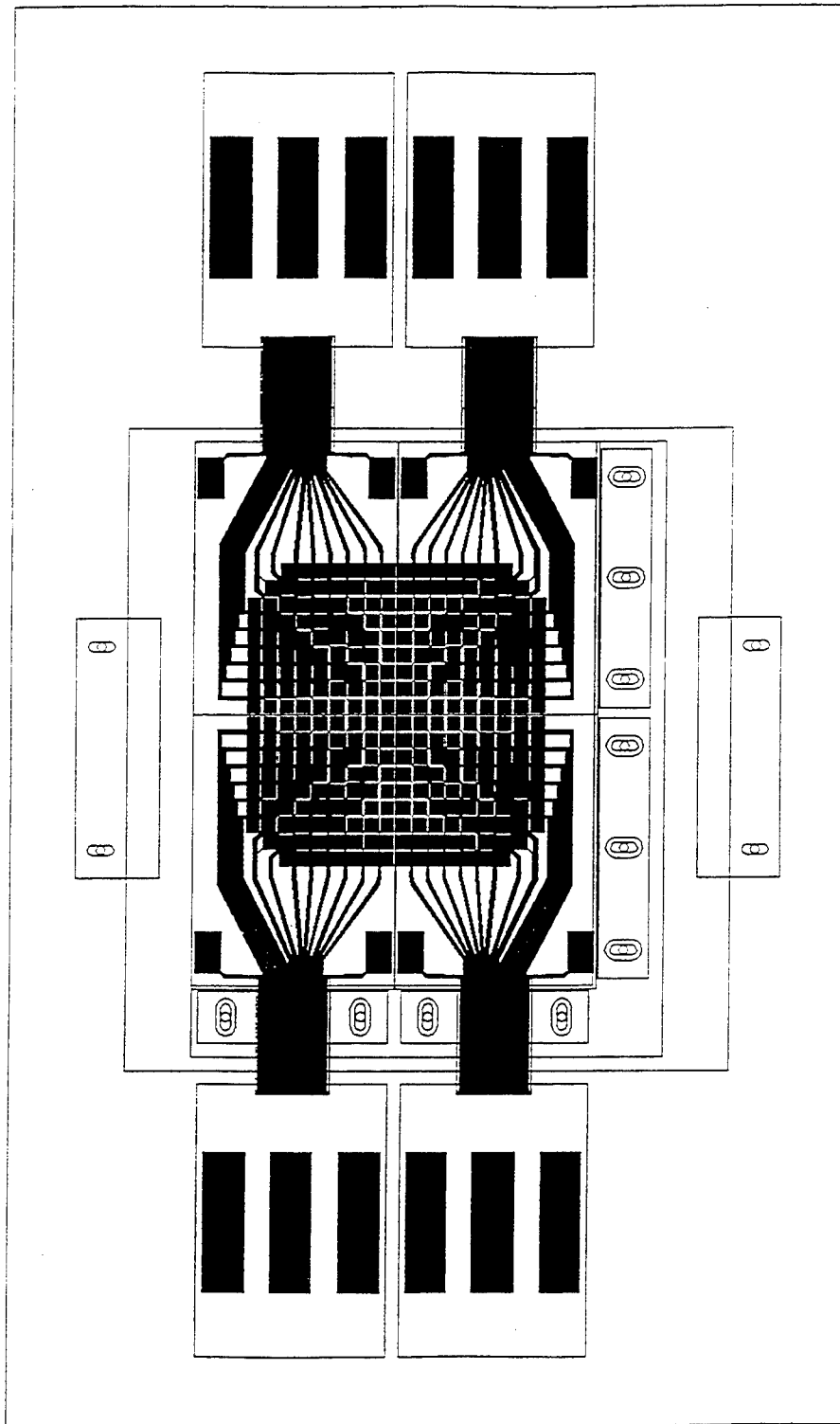
FIGURE 21. Front view of the demonstrator.

(a)

sample: 110393-3   11-04-93 17:10

100
Trmax: 56.57 %   10.8 : 1 @ 20.0 V

-UP-
Tr 56.6%
10 11.0
50 15.0
90 21.0
Sp 0.36
Op 4.62

-DN-
Tr 56.6%
10   6.0
50 10.0
90 18.0
Sp 0.67
Op 4.88

Sw Sec
%101.23

Uh 5.0
FoM 34.5
S↑ 8.1
S↓ 6.0

Transmittance

50

0
0   6   12   18   Volts   30   36   42   48

(b)

Tran=9.464 %   (/div)
tswp=0.239 Sec points=479
Trace Menu Active   11-04-93 Time: 17:10
Frame # 4-1   110393-3   X Range [0.66 - 0.90]

Trans

1Sample 2SvSmpl 3DskOff 4XZoom 5Retrac 6List   7Title 8Cursor 9Param 10Exit

FIGURE 22.   Performance of direct view formulation 110393-3.
(a) Transmittance vs. operating voltage.
(b) Time response to a squarewave driving signal.

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(a)
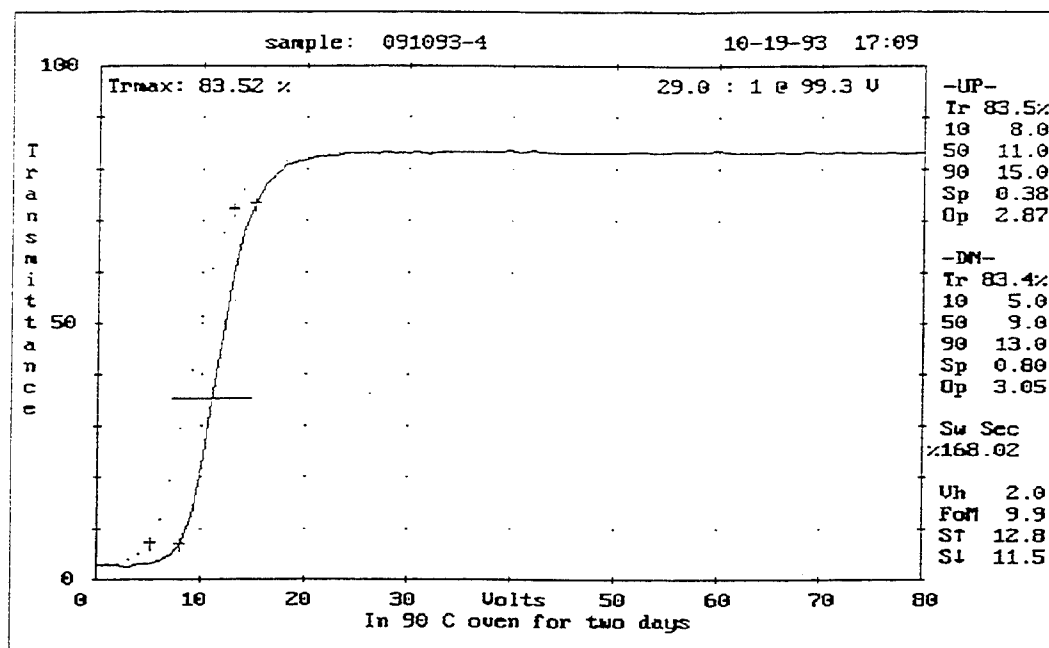
(b)
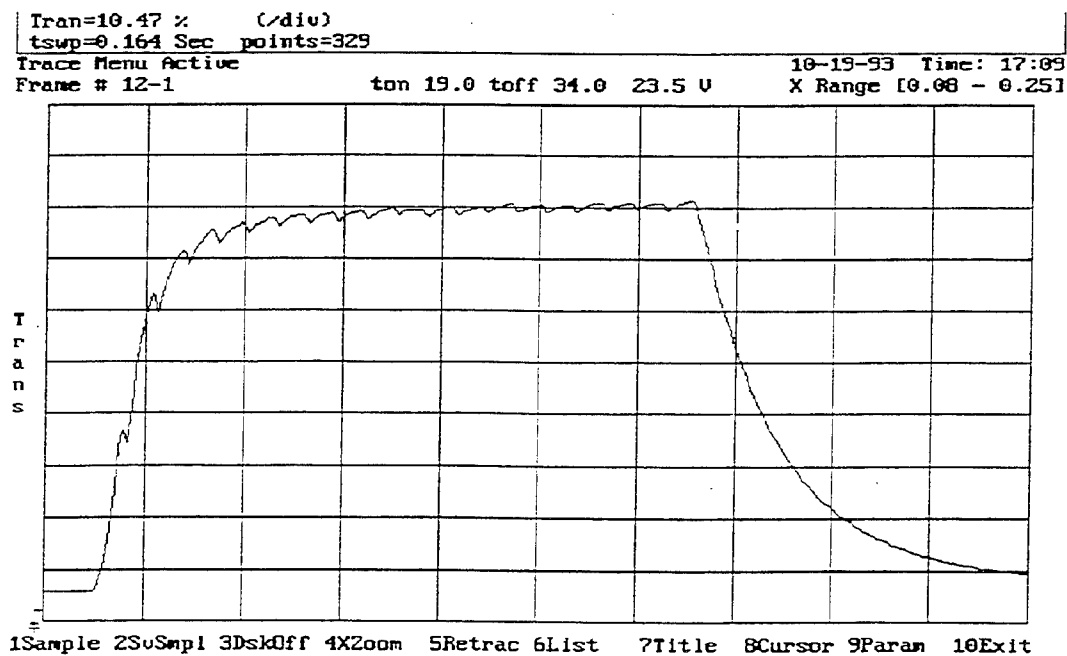
FIGURE 23. Performance of projection formulation 091093-4.
(a) Transmittance _vs_. operating voltage.
(b) Time response to a squarewave driving signal.

(a)
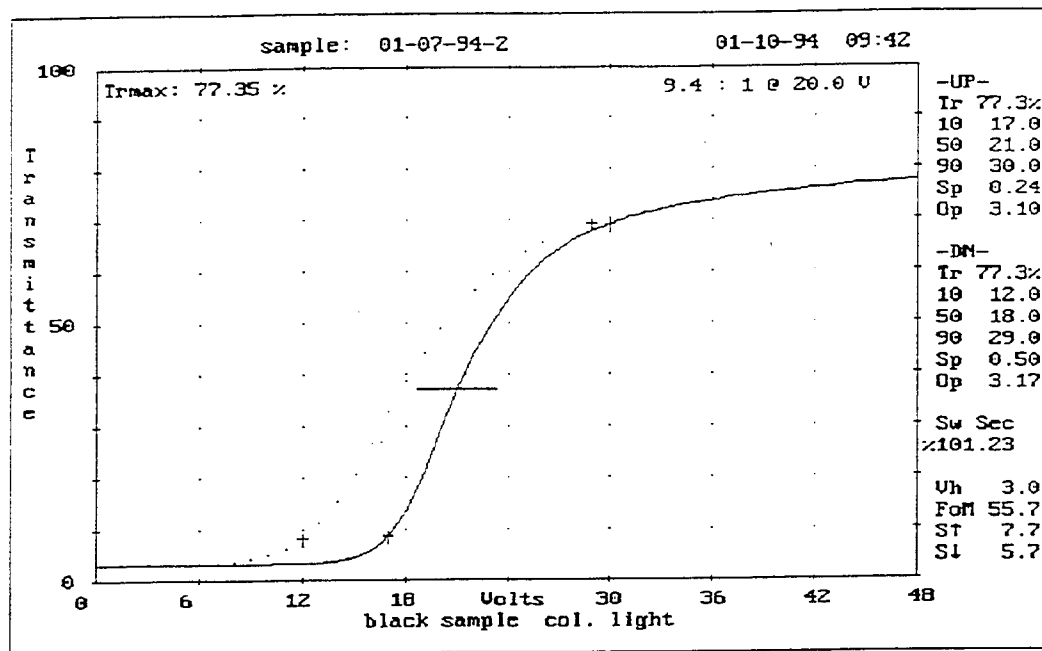
(b)
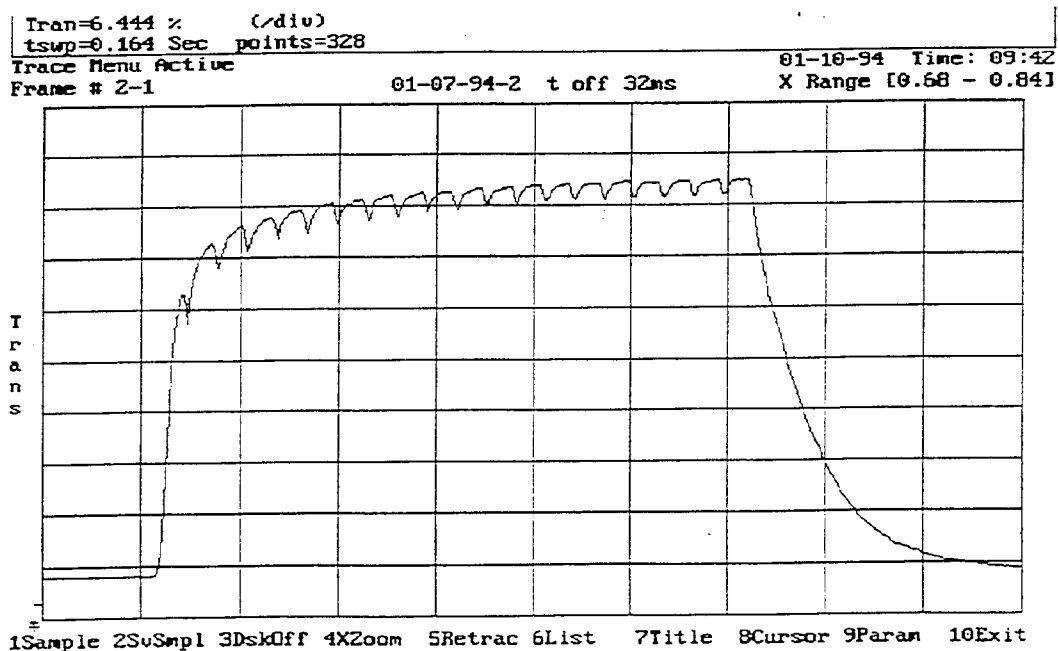
FIGURE 24.   Performance of reflection formulation 010794-2.

(a) Transmittance _vs_. operating voltage.

(b) Time response to a squarewave driving signal.

14. HYSTERESIS

Hysteresis, which is common for liquid crystal devices became
even more pronounced in PDLC materials. The hysteresis has an
adverse effect on gray scale accuracy. The target for this
project was the achievement of 0.1 V or less of hysteresis. This
would potentially allow a gray scale with barely noticeable
inconsistency.

The origin of hysteresis is not well understood. Asahi glass
chemists claim that it is caused by droplet to droplet
interactions, while Raychem people postulate that intradroplet
interactions cause the phenomenon (Figure 25). Visual
microscopic examination of larger droplets, as they are switched
ON by gradually increasing electrical field, supports the Raychem
theory.

We had planned to reduce the hysteresis of the system three ways:

    A)   Balance the Butyl/Isobutyl polymer content.
    B)   Addition of solid particles to the system.
    C)   Utilization of fluorinated polymers.

A)   The Liquid Crystal Institute had reported that the surface
alignment of Butyl Acrylates is radial:
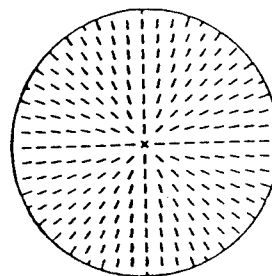
while that of Isobutyl is axial:
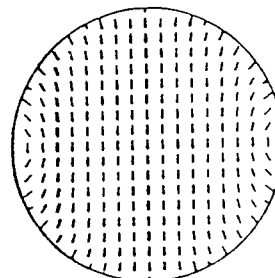
Asahi Glass: produces low Von, 0-0.1 V hysteresis UV cured PDLC. They attribute hysteresis to droplet - droplet interactions
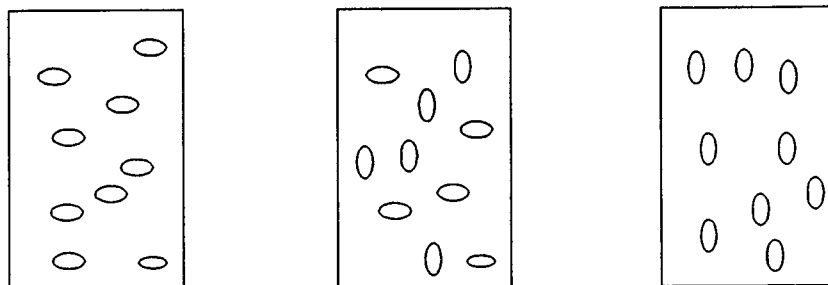
| High Hy | Low Hy | High Hy |

Partially aligned droplets

Raychem: low hysteresis is found in small smooth wall PDLCs. High hysteresis is found in irregularly shaped droplets.
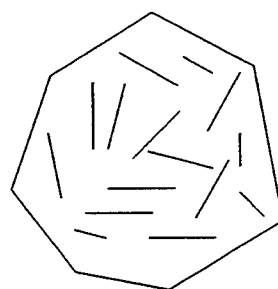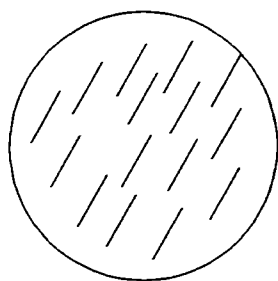
Seen microscopically in 3-5 μm droplets

FIGURE 25. Techniques for achieving low hysteresis.

If hysteresis is related to surface forces, one might expect that by achieving a near balance of the two tendencies within a droplet, a source of hysteresis would be eliminated. When the applied field is reduced, the relaxing LC molecules would not be "confused" by balancing forces which draw them into nematic alignment versus polymer interface alignment. Certainly, some of our thermoplastic Butyl Acrylate work and Butyl/Isobutyl copolymer samples exhibited low hysteresis (~1 V). However, to produce stable samples with hysteresis below 1 V was not possible.

B)   If, as Raychem reported, small uniform droplets have less hysteresis than large irregular droplets, then the addition of solid particles to the system should change the number of defects in the droplets and induce a change in hysteresis. Small amounts of additional defects would increase the hysteresis, while large amounts of defects may decrease it by creating such small domains that the activation energy to move them would be very small.

C)   Fluorinated Polymers: "Hysteresis appears to be a property that can be influenced by the choice of polymer. Recent work has shown that the addition of a fluoracrylate can reduce hysteresis. Polymers such as PN393 have been formulated so as to give low hysteresis, however the amount of hysteresis found varies depending on the curing condition; as yet it has not been possible to control this and the values of 0.1 to 1.5 V are typical – some films are better and some are worse." (David Coates, E. Merck Ltd.)

Some of our more successful experimental results are shown in Figures 26, 27, & 28. Simply manipulating the Butyl/Isobutyl acrylate ratio never gave us less than 1 volt hysteresis. Sample 071393-4 was made from a formulation that contained both fluorinated polymer and silica particles. While the hysteresis is near zero when the sample is a few days old, it will increase to over 1 V after oven aging at 60°C.

The effect demonstrated in Figures 27 & 28 relates hysteresis and frequency. Sample 080993-3 would normally show positive

hysteresis when tested at constant frequency. When the downward voltage sweep is done at <u>higher</u> frequency, however, the hysteresis will disappear or become negative, indicating a dependance of refractive index on frequency. Sample 081093-5 displays the opposite effect, however. When the downward voltage sweep is done at <u>lower</u> frequency, the hysteresis is reduced. The polymer used in sample 081093-5 is fluorinated and that is the only polymer which had that behavior. This appears to be consistent with work done by D. Coates and quoted earlier in this section.

We believe that the results of this work indicate that it may be possible to predictably eliminate hysteresis. The method would involve a designed experiment to test various ratios of the normal polymer (Figure 27) that has a positive frequency-hysteresis relationship with the fluorinated polymer (Figure 28) which displays the negative relationship.

One would expect to find a point at which there would be nearly zero hysteresis at constant frequency where the two hysteresis-frequency phenomena cancel each other. We did attempt a number of this type of experiments with the different frequency responses combinations. The constraints of time and the shortage of key polymers caused us to stop this work before it was satisfactorily completed. A project of the scale required to settle the issue would involve preparation of eight to twelve fluorinated polymers and then using them at a number of levels in PDLC formulae. The polymer synthesis work is costly because the fluorinated polymers are expensive and they react slowly in the polymerization reaction. Two to three man-years of time would be needed to perform the laboratory work and product testing.

(a)
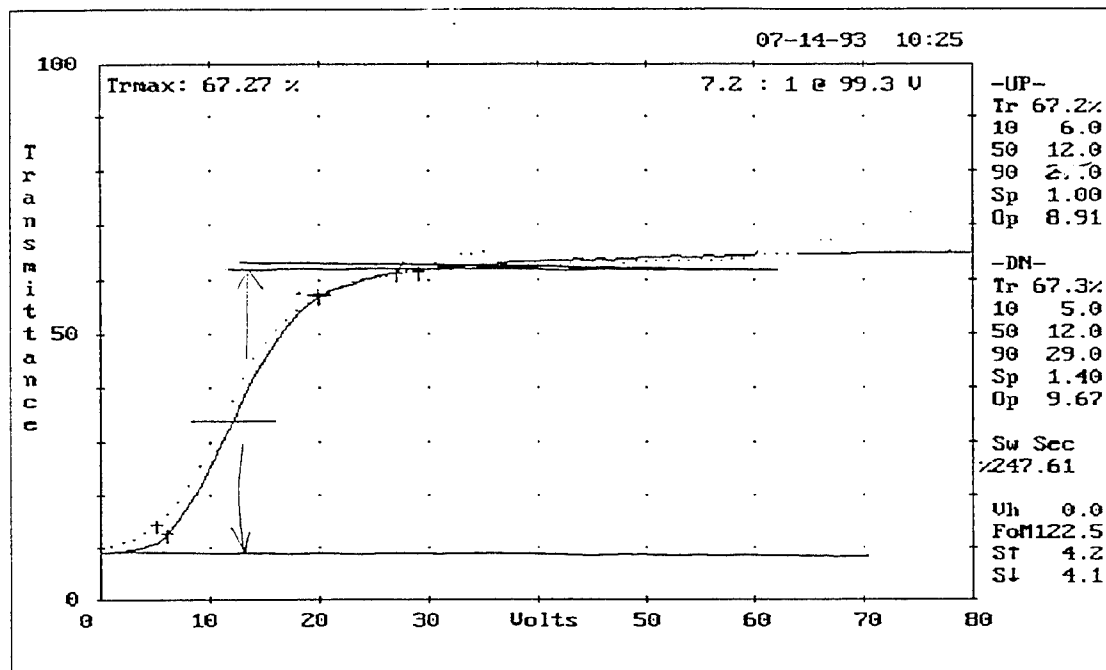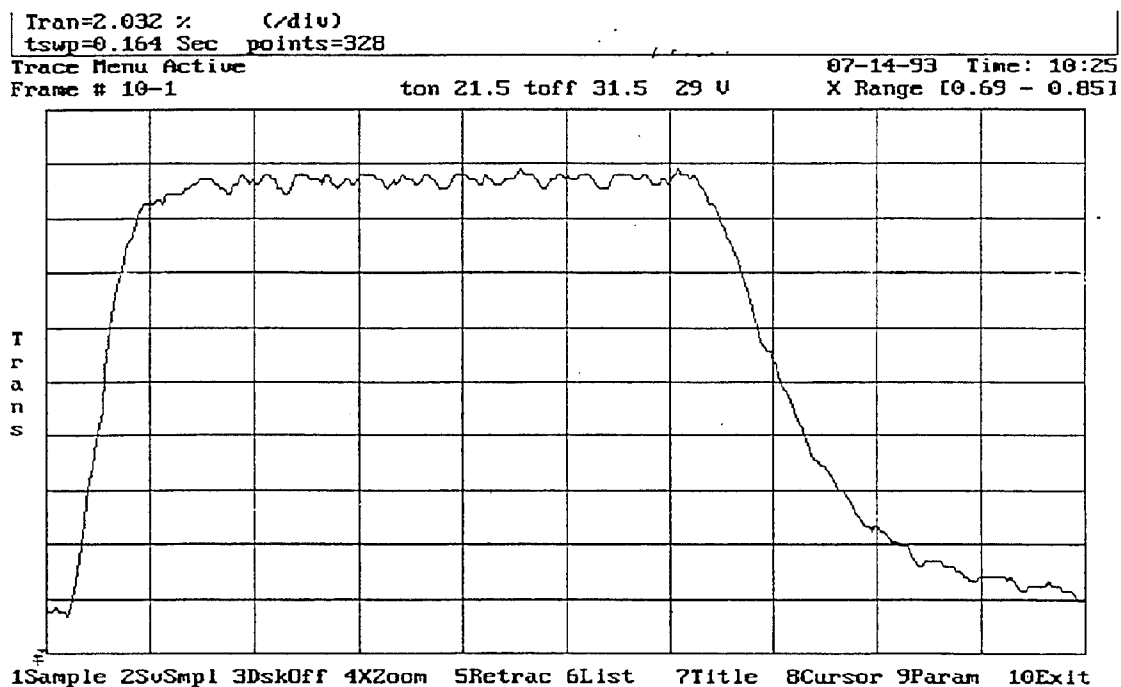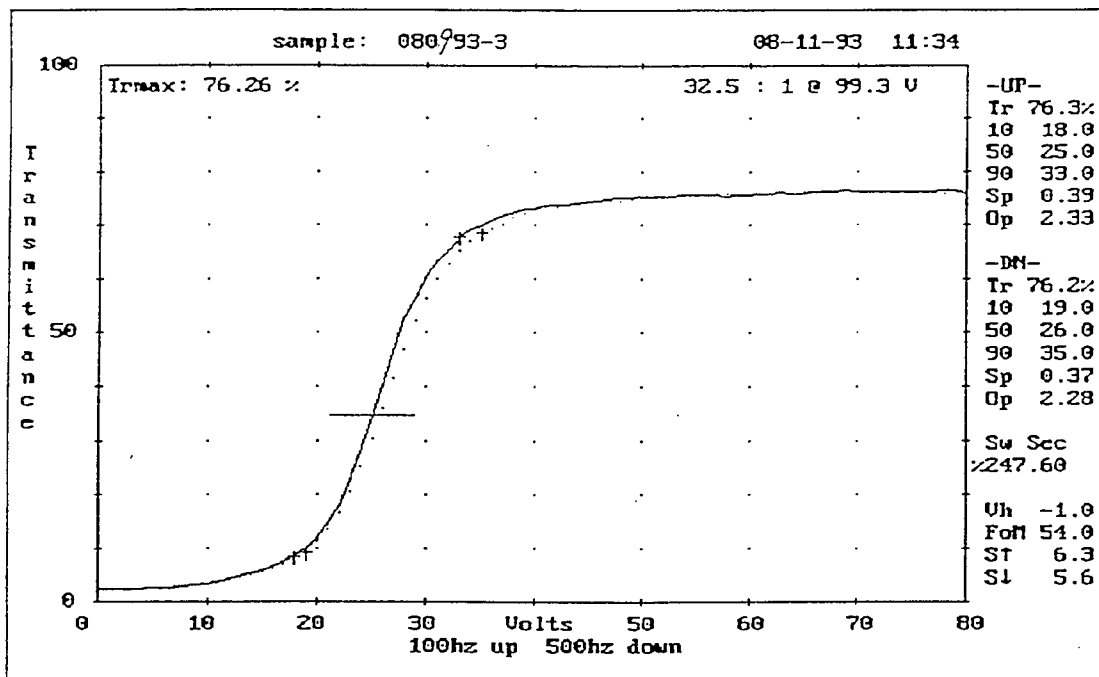
(b)

FIGURE 26.   Performance of low hysteresis formula containing fluorinated polymer and silica particles (sample 071393-4).

(a) Transmittance _vs_. operating voltage.

(b) Time response to a squarewave driving signal.
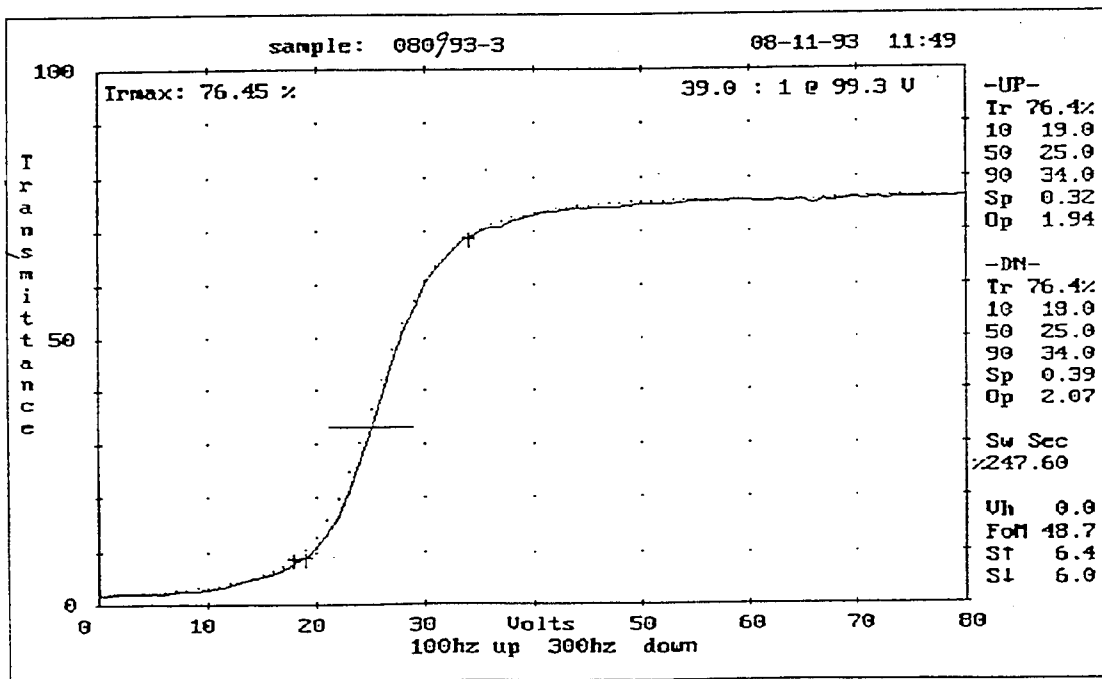
(a)

(b)

FIGURE 27. Reduction of hysteresis utilizing a higher frequency driving signal during the downward sweep (sample 080993-3).
(a) 100 Hz upward sweep, 500 Hz downward sweep
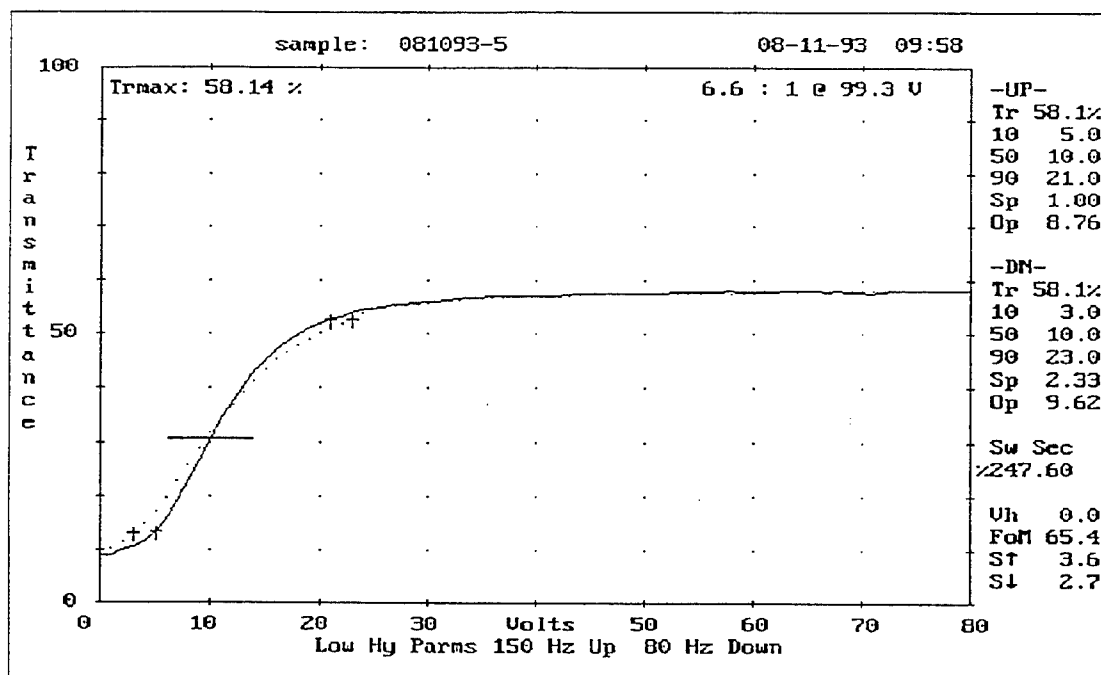(b) 100 Hz upward sweep, 300 Hz downward sweep

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FIGURE 28. Reduction of hysteresis utilizing a lower frequency driving signal during the downward sweep (sample 081093-5) : 100 Hz upward sweep, 50 Hz downward sweep.

15. ENVIRONMENTAL STABILITY

The main concern about stability of PDLC stems from the fact, that in the intended Magnascreen application (tiled display), the edges of PDLC layer are unprotected by the seal and thus exposed to the environment. In our earlier experience (Contract MDA792-C-90-0032), preceding the onset of this program, the edges of our test display modules brightened (faded out) within days to weeks when continuously operated. The problem was traced to decomposition of the black dye components initiated by UV light and accelerated by the presence of an electrical field, combined with humidity in the ambient air.

Two setups were used for testing the PDLC edge stability:
      a) Fluorescent backlight box, Phosphor SP 41, 1600 fL.
      b) Heraeus Suntest CPS UV chamber.
The samples under test were continuously maintained in an ON condition by 50 V ac voltage and monitored at regular time intervals for visual edge deterioration. Samples under test were compared with a standard for signs of fading. Though this evaluation was subjective, the test basically simulated the impact of edge fading on a human observer, the criterion being the just noticeable difference, a quantifier commonly used in evaluation of displays.

The backlight box simulates the conditions encountered in a typical indoor display application (office environment), where the level of UV irradiation of the PDLC is determined by the light generated by the fluorescent tubes.

The Suntest chamber is used for accelerated tests for outdoor applications, as the light generated by its Xenon lamp simulates the solar spectrum.

Though the tests are still in progress, the following results seem to hold:
- Black dye mixtures Mitsui 8426 and LaRoche(B2,B3,Y2,R4+R) do not show any detectable degradation at the edges of the samples prepared with wide spectrum of acrylics, when tested on the fluorescent box (1200 hours).

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- All tested samples faded in the Suntest chamber across the entire sample area, though the loss of optical density was accelerated at the edges. Typically, the fading at the edges became noticeable after 100 h of testing.

We conclude that the acrylic polymers, developed in the course of this program, provide sufficient protection of LC droplets from moisture in the ambient air, and when combined with UV stable dyes the resulting PDLC formulae will not exhibit the "edge effect" in typical indoor display applications.

However, the results from the accelerated test suggest that under extreme conditions the edge area deteriorates faster than the bulk of the PDLC and some form of edge protection (impregnation?) should be developed in the future to improve long term stability of tiled displays.

All PDLC samples were tested for performance degradation after being exposed to 90°C for 48 h. The results were reported throughout this report in performance tables shown in several Sections under the column Oven (see also Appendix A). The samples which fared well in the oven test were also exposed to −40°C for 48 hours. We neither detected change in performance nor mechanical failure (delamination, cracks etc).

We conclude that the performance of the optimized PDLC formulation will not be affected by storage within the tested temperature range of −40°C to +90°C.

16. COATER UPGRADE

16.1 DESIGN SUMMARY

Concept
The coater design objective was to provide a laboratory coater/laminator to lay down an accurate, uniform coating of PDLC material on a plastic substrate, and to laminate this composite film onto a rigid substrate blank. High uniformity of coating is essential for modular displays, as the human eye is very sensitive to abrupt changes of light color or intensity. These abrupt changes can occur at adjacent modules interfaces for various reasons, but the ones originating from non-uniformity of display medium are the most difficult to correct.

The redesigned machine is an upgraded design of existing equipment at Peregrine. The machine allows coating and laminating of solvent based complex urethane materials. As such, the design objectives incorporate; ease of use, easy set-up and cleaning, ruggedness, repeatability, conservation of materials, and ease of service.

The machine layout, as shown in Figure 29, allows polymer dispersed liquid crystal formulations to be precisely applied to the side of plastic film coated with a thin transparent conductive layer of ITO, then dried, and finally laminated to a film and/or rigid substrate. The machine was designed for clean room operation, at Peregrine Optifilm Inc., and may be broken into three major sections of, Coating, Drying, and Laminating.

Coating
The main coating head, labeled as (C1), is a computer controlled linear extrusion head. The PDLC coating is precisely metered by this head onto a ITO/plastic film substrate at a rate consistent with the velocity of the film substrate. The head is supplied by a fluid dispenser system, positioned below, (PUMP, FILTER), which filters and dispenses the PDLC formulation through the head for a uniform coating thickness laydown. This head may be controlled to give a continuous or multiple zone cast, with essentially no

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material waste. Head design allows very uniform coating thickness laydowns from 4 to more than 26 microns.

Positioned adjacent to this head , labeled as (C2), is a secondary knife over roll applicator which may be used for additional metering and smoothing of the coating as required. Plastic film is unwound at a controlled tension past C1, C2, coating heads from an unwind supply stand below the coating heads.

The coating operation will be completely controlled in operation by an internal computer (refer to Figure 30, block diagram). This computer monitors and controls the key coating parameters which control film thickness and uniformity. Among these are dispense rate, substrate velocity, extrusion slot orifice geometry, and temperature.

Drying
With a variable speed drive, the coated film is drawn into a controlled environment drying oven. Here, the coating is partially cured (solvent evaporation), by heated air flow at a controlled temperature. The length of the drying chamber, oven, has been determined to allow optimum film properties to be developed before lamination.

Air into the oven is filtered to remove particulate contamination by HEPA filter units. Within the oven, nozzles direct the air flow uniformly across the web width. The air flow rate is controllable by variable speed supply blowers. Electrical heating units provide uniform dry air temperatures up to 110°C.

Lamination
Two laminators are provided, as shown on Figure 29 (L1), film to rigid substrate, and film to film lamination (L2).

In the case of film to rigid lamination, a rigid substrate blank (loaded within a jig) is fed through the (L1) lamination station (right to left). By application of pressure, the PDLC film is laminated onto the substrate.

In the other case of film to film lamination, a second film substrate or release liner may be applied to the coated web at the (L2) lamination station. After this lamination, the thin film laminate would be rewound onto a take-up roll, shown in position below the laminator.

Lamination station (L1) will provide for pressure and speed control, and station (L2) allows for pressure, as well as, temperature control at the lamination nip.
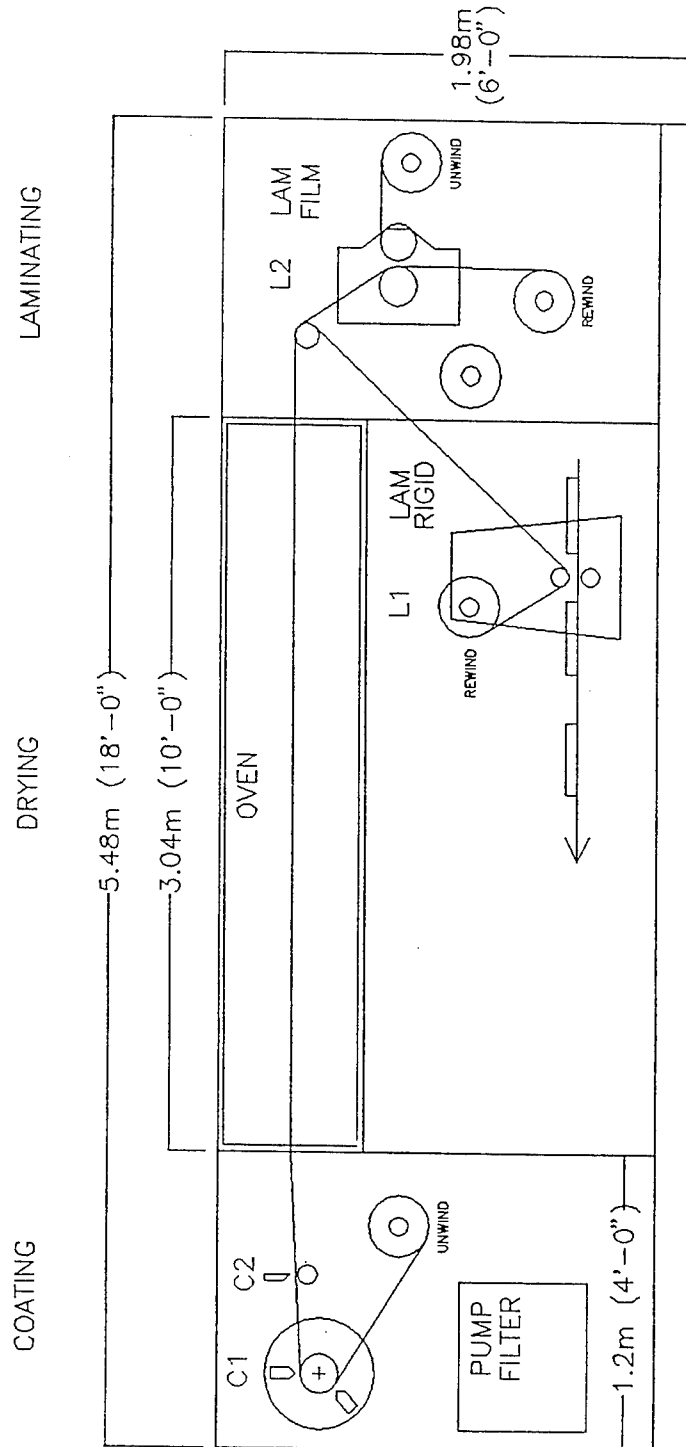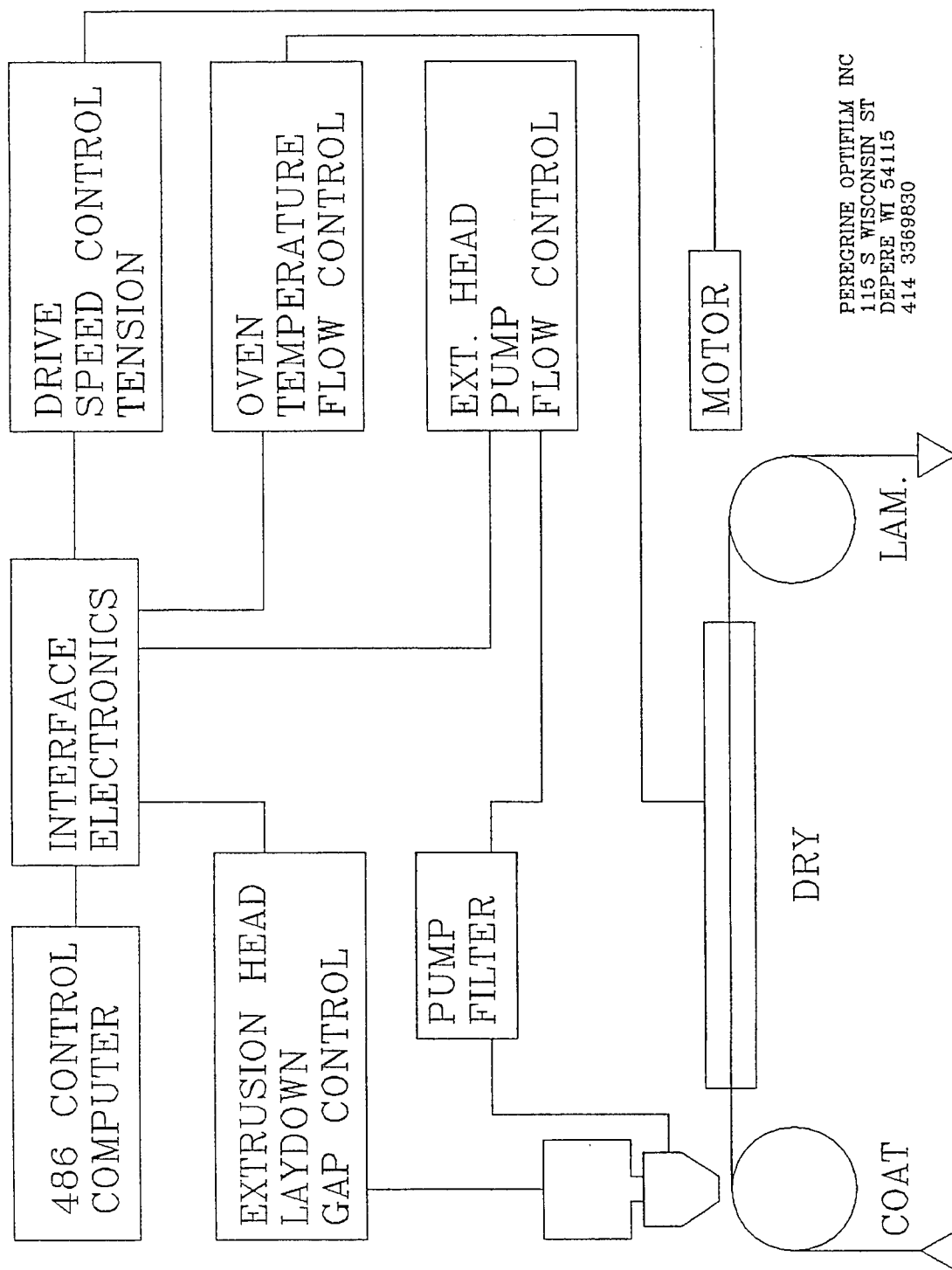
The full synopsis of the redesigned coater is shown in Table 20.

FIGURE 29. Coater layout.

FIGURE 30. Control diagram.

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TABLE 20.   Coater Synopsis

WEB MATERIAL   Polyester 45-175 μm (2-7 mils)
REAM SIZE   300 m^2 (3000 Sq. Feet)
WEB WIDTH   30 cm to 40 cm
                                   (12" Norm., 16" Max.)

LINE SPEED   68 cm/min to 1148 cm/min
                                   (2.3 ft/min to 38 ft/min)

NUMBER OF SIDES COATED   1
COATING   Liquid Acrylic with LC.
DRY COAT THICKNESS   12 to 20 μm (0.5 to 0.8 mils)
WET COAT THICKNESS   45 to 60 μm (2 to 2.5 mils)
PERCENT SOLIDS   60 to 70%
SOLVENT   Toluene/Ethyl Acetate
COATING HEAD   Slot Die Applicator
                                   30 cm wide (12 in.)
                                   45 μm gap (2.0 mil)

COATING PUMP   Meter Displacement (Gear)
                                   1.722 cc/Revolution

LAMINATOR FILM   Heated Steel/Rubber Roll
LAMINATOR RIGID   Rubber/Rubber Roll

DRYER DIMENSIONS

AIR NOZZLE LENGTH   Laminar Flow Filter
NUMBER OF ZONES   3
OVERALL DRYER LENGTH   5 m (16 Ft.)
OVERALL DRYER WIDTH   0.9 m (36 In.)
OVERALL DRYER HEIGHT   1.3 m (48 In.)

MATERIALS OF CONSTRUCTION

DRYER INTERIOR   Steel
DRYER EXTERIOR   Mild Steel
AIR NOZZLES   Laminar Flow Filter
HEATER PLENUM INTERIOR   Steel
EQUIPMENT FINISH   Parker Industrial

16.2 COATER START-UP

With the completion of the mechanical changes on the coater-laminator (see Figure 31), a variety of test runs were made to "debug" its operation. A number of problems were discovered and resolved.

- The original Viton™ pump seals had to be replaced with the more solvent-resistant Teflon™.
- The pump was also drawing air into the fluid system through a lubrication port which was subsequently sealed off.
- A pressurized feed container was added to eliminate other sources of air entrainment to the feed system.
- The original die slot was too wide to control coat weight down to the 10 micron range, so the head was "shaved" to a slot opening of 45 microns.
- The gear ratio of the drive system was increased by a factor of three in order to reduce the web speed and allow for more drying time before lamination.
- A hydraulic lift was added to the coating head in order to allow it to pivot around the backing roller. This allows air to work out of the head prior to coating and the use of more of the coating which can be retained in the die cavity.
- Wedge blocks were added to the die cavity in order to produce a more uniform fluid flow across the face of the slot.

Samples were cut at 30 cm intervals from an approximately 2 meter long coated section. They were tested for electro-optic uniformity. Results are reported in Table 21. Five repetitions were done on each and the range indicates the systematic error in the test equipment. The sample variation is then approximately ±5% at this stage in the start-up. Though the target value of ±2% was not met, we are confident it can be reached with continued effort.

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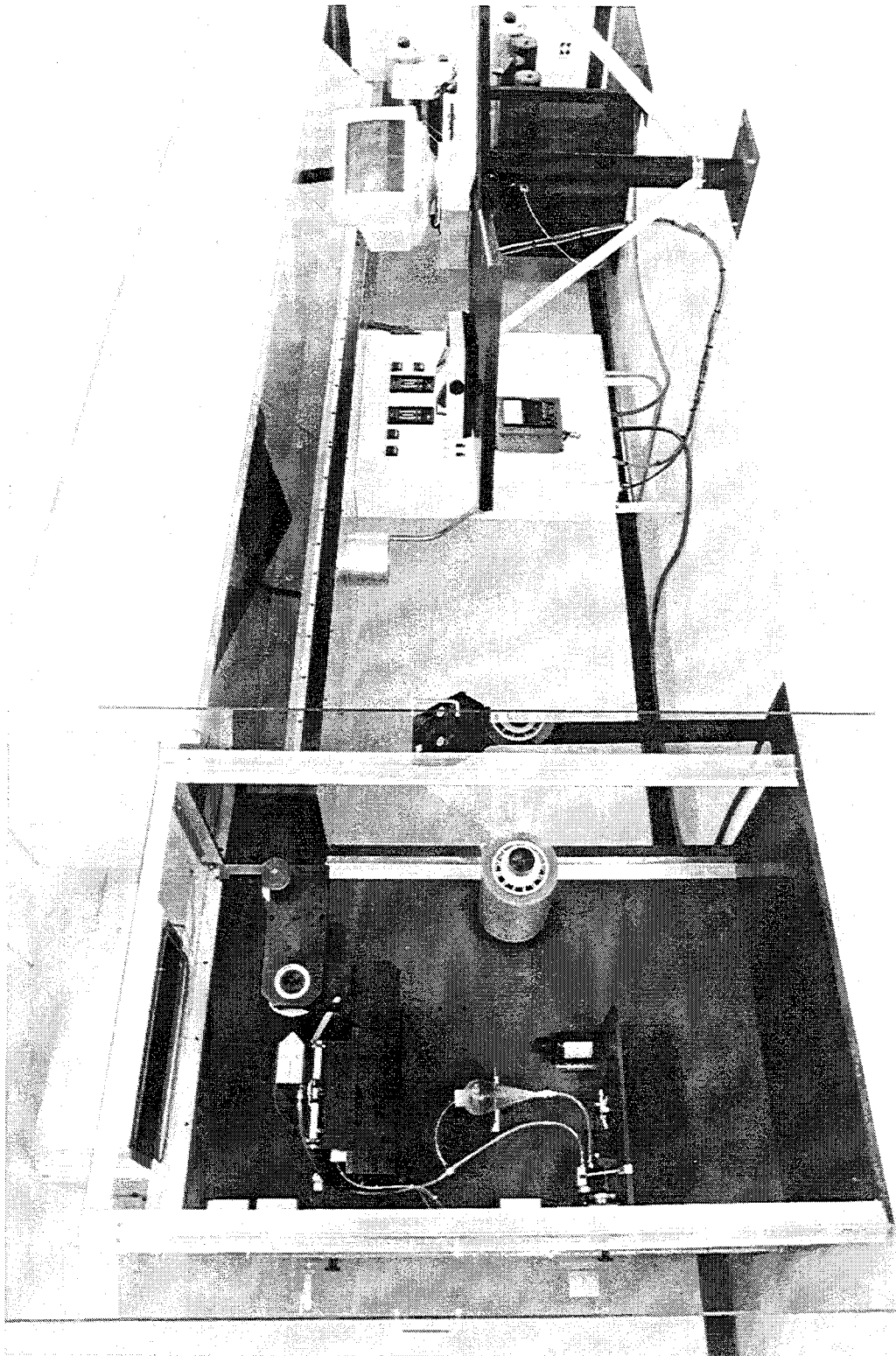**FIGURE 31.** Redesigned coater.

TABLE 21. Uniformity of Coated Web

<u>TRANSMITTANCE</u>

SAMPLE	<u>T min</u> [%]	<u>T max</u> [%]
1	5.5 ± 0.1	74.1 ± 0.6
2	5.0 ± 0.2	76.1 ± 1.6
3	5.2 ± 0.2	78.3 ± 1.6
4	5.0 ± 0.1	78.3 ± 1.6
5	5.4 ± 0.1	79.9 ± 1.6

VARIATION
BETWEEN SAMPLES   ± 5%   ± 4%

17. RESULTS SUMMARY

Concrete achievements are reported in the sections describing the efforts to improve various properties of PDLC. In this section we report on generalized findings which, in essence, are the established links between chemistry and PDLC performance:

- Butyl Acrylates tend to operate at lower voltage than Methyl Acrylates.

- Acrylics containing Silicone tend to operate at lower voltages than Hydrocarbon Analogs.

- Fluorinated Polymers tend to produce higher drive voltage but lower hysteresis PDLC materials.

- Butyl Acrylate matrices have higher ON transmittance than Methyl Acrylates.

- Some Fluorinated polymers can reverse the refractive index - drive frequency relationship of normal liquid crystals.

- Halogenated liquid crystals tend to have low solubility in Acrylic polymer, and form fast, high voltage PDLC materials.

- Simple extraction techniques can substantially improve PDLC ingredients resistivity.

- Acrylic matrices tend to form more stable dyed PDLC materials than epoxy based systems.

The incorporation of most of these findings into a single formula produced the optimized PDLC material D-14 (Matrix III). Its performance is reported in Table 22, where it is compared with initial and target performance values. The chemical composition of D-14 is reported in Table 23.

After debugging the redesigned PDLC coater and some development effort, highly uniform PDLC films were reproducibly casted on ITO coated mylar foil. These preliminary results demonstrate that

PDLC can be economically produced for large area, tiled displays by the solvent-induced phase separation technique.

TABLE 22. Performance of Optimized PDLC Formulation

PARAMETER	INITIAL[@]	FINAL	TARGET
Operational Voltage (V_{90}), V_{rms}	60-80	17.0	< 15
Response Times (t_{ON}, t_{OFF}), ms	50;100	29;45	< 20
Contrast Ratio	2 : 1	10.9 : 1[*]	8 : 1
Transmittance (@ V_{90}), %	30 -40	65	60
Resistivity (DC, aged)	10^{10}-10^{11}	~10^{12}	>10^{12}
Hysteresis (δV_H), V	5-10	3.0	0.1
Temperature Range, °C	unknown	-40,+80	-30,+70
Uniformity (of EO performance)	± 3%	± 5%	± 2%
Stable to edge	No	Yes[#]	Yes

[@]   Initial values indicate performance of typical PDLC
      formulations available to Magnascreen prior the initiation
      of this program

[*]   For non-Lambertian diffuser (Rohm-Haas L Plexiglas, 1 mm
      thick).

[#]   After 1200 hours of continuous operation on fluorescent
      backlight 1600 fL.

TABLE 23. Chemical Composition of the Optimized PDLC
              Formulation (D14, Matrix III)

Polymer:	83-1 / 83-13	.3 pt
	83-1 / 93-18	.3 pt
Liquid Crystal:	510/E7	.6 pt
Additives:	FLNA/PHOBU	.03 pt
Black Dye:	S 426	4.6% of LC
Additives:	CS 2600/2175	.06 pt

18. CLOSING REMARKS

This development program has pursued finding the PDLC formulation having parameters which meet all the target specifications. The most important parameters include contrast ratio, transmittance, response times, operating voltage and hysteresis. While substantial improvements were made, it is still not possible to synthesize a single PDLC product which would fully comply with all the target specifications.

Results from the early phase of the program indicated that the normal, undyed PDLC materials can be optimized to fully satisfy the target specifications (with the exception of hysteresis - see below). The addition of the black dye, which is necessary for direct view displays, however, has been shown to have an adverse effect on switching speed, operating voltage and hysteresis. We have not been able to completely overcome all the difficulties caused by the introduction of the dye and certain compromises in performance characteristics had to be made, especially in following categories:

- Transmittance vs. Contrast Ratio
- Voltage vs. Response Times

The current best formulation, which performance characteristics are shown in Figure 23, features a balanced compromise of the parameters.

It was demonstrated, however, that it is possible to have a dyed PDLC formulation with parameters which satisfy or exceed one or more of the target values. These formulations, which are a byproduct of this developmental effort, may be useful in other display applications such as signage or reflective displays.

Given the difficulties experienced during the optimization process of the dyed PDLC, we feel that the prospects for further improvements of dyed materials are limited. Even though the target value of contrast ratio 8:1 has been achieved, about 30:1 is required for a full color display. It is unlikely that PDLC with such high contrast ratio can be developed without

significantly sacrificing ON transmittance i.e., brightness of display. The results of this research clearly point out that the undyed PDLC materials, typically used in projection devices, have much better chances for commercial success, especially when the hysteresis problem is successfully resolved.

Despite substantial improvements in almost all targeted PDLC parameters, hysteresis on T-V curve was improved only marginally. Increased effort to address this stubborn problem during the course of this program, yielded hysteresis values which are still about one order of magnitude larger than the target values. Such large hysteresis precludes utilization of PDLC in applications where analog gray scale is required. The reason for insufficient improvement of the hysteresis is attributed to two facts:

- no strong link between PDLC chemistry and hysteresis has been found during this program.

- there is no established theory explaining the origins of the hysteresis phenomenon.

A new approach, preferably based on understanding of the phenomenon in PDLC materials, is needed before substantial improvement of the hysteresis can be expected.

APPENDIX A.   DEFINITION OF PERFORMANCE PARAMETERS

This appendix lists parameters used for evaluation of the PDLC performance in this report.

Operating Voltage V_{ON}   defined as V_{90}
Hysteresis V_H also called Hy is determined from T-V curves as a voltage difference between up and down sweep curves at 50% transmittance level.
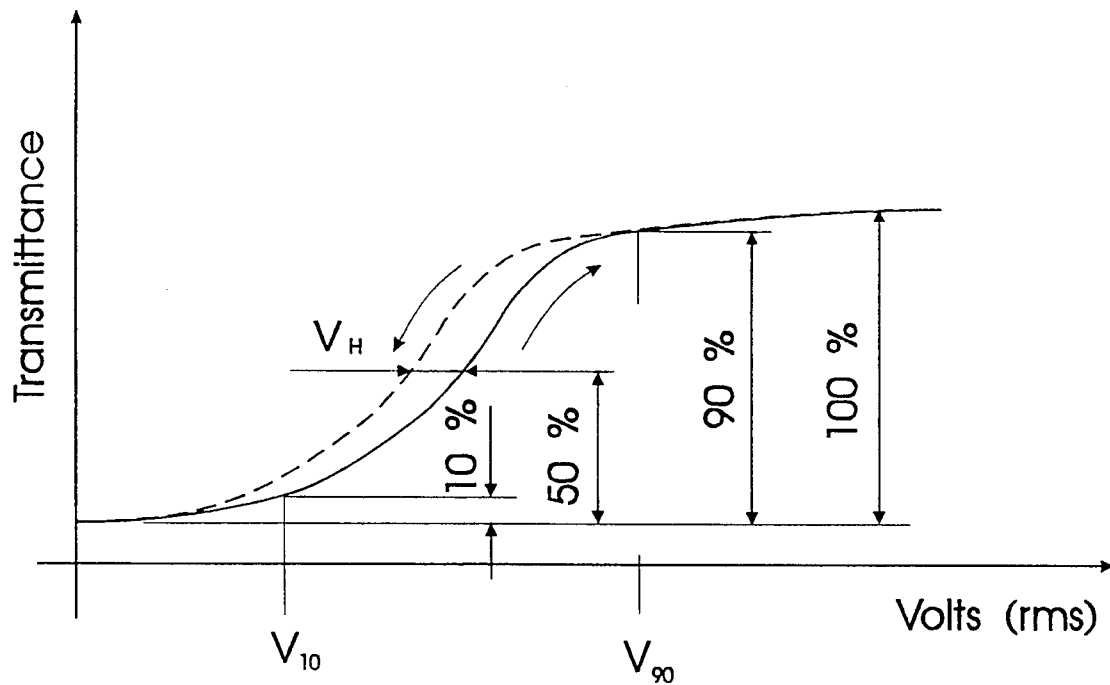

Note: Transmittance at 0 V is referred to as T_{min} and called opacity. Transmittance at V_{90} is referred to as T_{max}.

Response times t_{ON} and t_{OFF}, also referred to as switching times, "on" or "off" times.
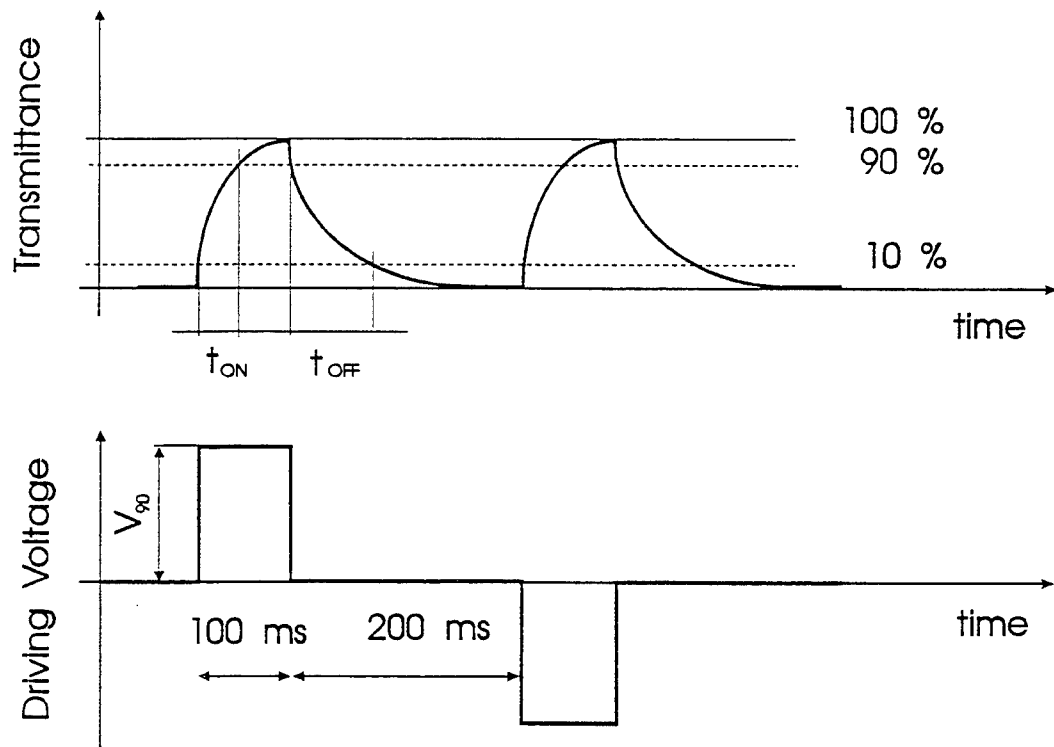
Charge Holding Ratio also referred to as Voltage Holding Ratio or simply HR. It is determined from optical response to sample and hold signal.

Charge holding ratio HR (%) = 100 x V_{OUT}/V_{IN}
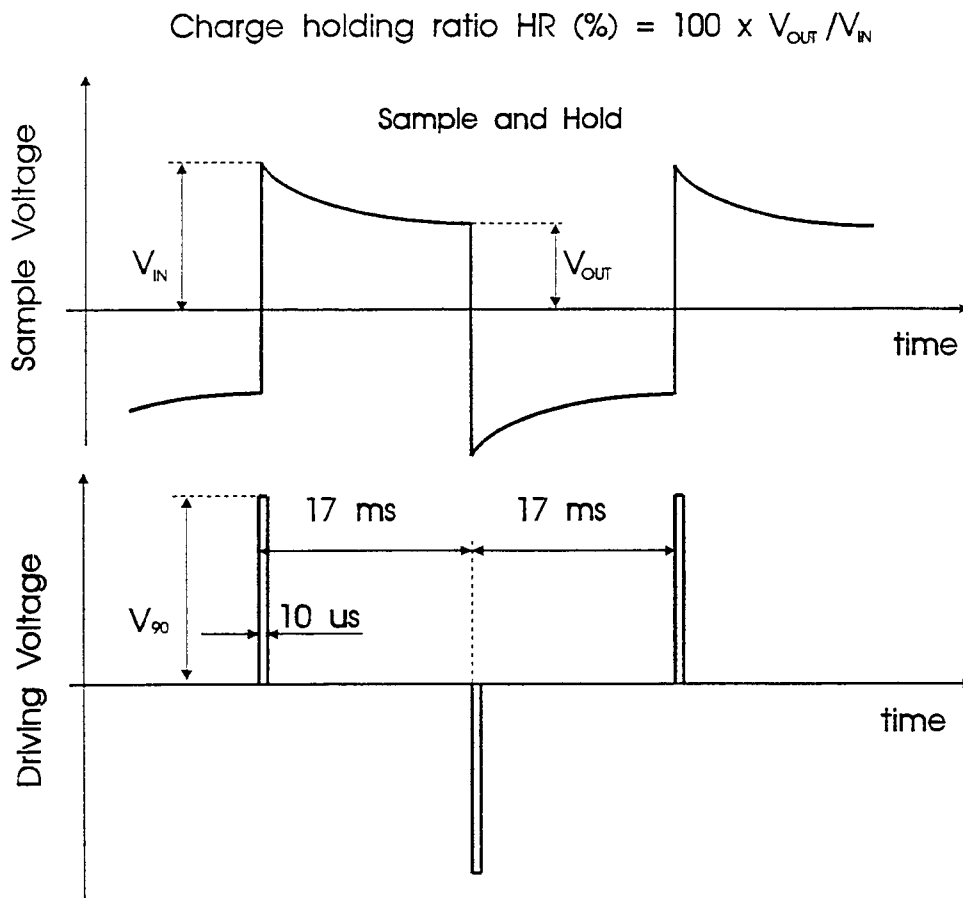
HR can be used in lieu of resistivity under defined conditions. For exponential decay of voltage across the PDLC layer (having relative permitivity of 8) and a refresh rate 60 Hz, the corresponding values are:

ϱ [Ω.cm]	10^{10}	10^{11}	10^{12}	10^{13}
HR [%]	8.8	78	97.5	99.8

The sample performance after **oven aging** at 90° C for 48 hours are indicated by the following scale:

GOOD+   Improvements in performance
GOOD   No significant change in performance
FAIR   Slight degradation in performance
POOR   Severe degradation in performance

Figure of Merit ,also labeled as "FOM" is the result of the equation:

$$FoM = \frac{V^2_{on} \cdot T_{min}}{80 - V_{on}}$$

It is a simple way to measure the relationship of the turn-on voltage, V_{on}, to the opacity, T_{min}. Samples that are generally believed to contain small droplet structures of less than or equal to 1 micron, or samples that are thicker tend to have a low T_{min} but high V_{on}. A low number for the FoM calculation will then indicate a favorable combination of drive voltage and opacity.
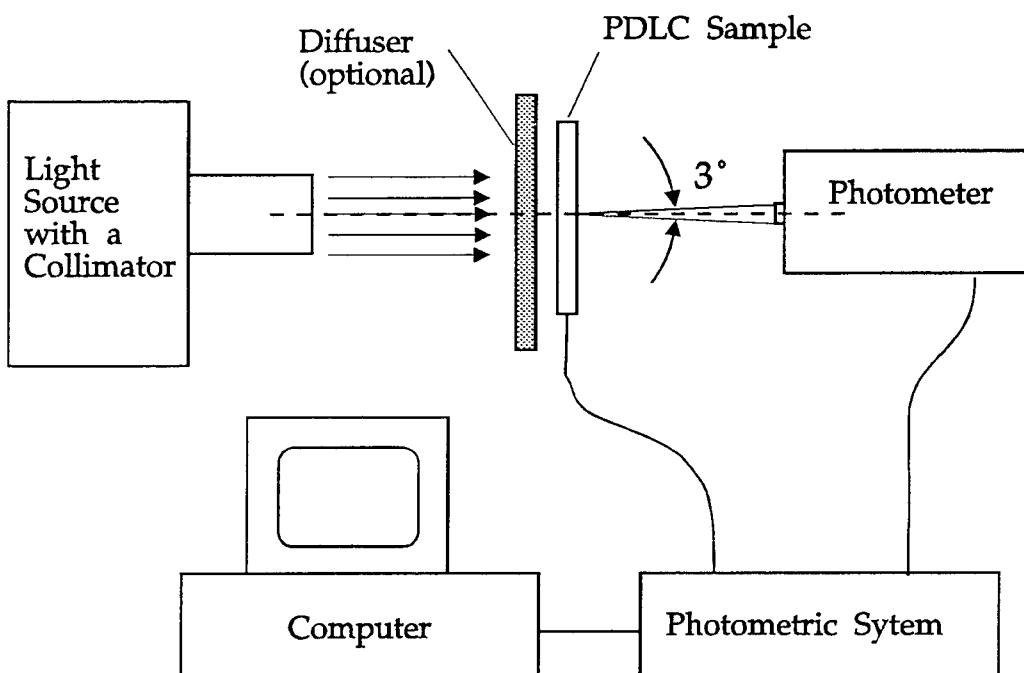
Licrilite Mixtures for Use over Active Matrix Substrates

The virtues of using a PDLC film in projection devices especially for projection televisions has been described by various research groups.[1,2,3]

For this application, not only is a high birefringence required to help produce a high contrast ratio, but it is also essential that the system has a high holding ratio. For TN active matrix liquid crystal mixtures the requirement is usually that the liquid crystal should have a stable high holding ratio of >98%; the same criterion has been applied to the mixtures being developed for active matrix PDLC use. TL203 contains some cyano compounds and its holding ratio after UV irradiation is lower than TL202, TL204 and TL205, which contain only very stable SFM compounds. In 10mmthick cells a contrast ratio of 30:1 is usual for TL202 but for TL204 and TL205 contrast ratios of over 150:1 have been measured in a suitable polymer such as PN393.

MERCK Ltd

PDLC/TFT Mixtures

Mixture:		TL202	TL203	TL204	TL205
Mpt	[°C]	+22	+13	-1	Not Frozen
S-N	[°C]	+1	<-20	-6	<-20
N-I	[°C]	+83	+77	+92	+87
Viscosity (cSt)	20°C	37	37	43	45
$D\epsilon$	(1 kHz, 20°C)	+6.1	+11	+4.8	+5.01
ϵ_{11}	(1 kHz, 20°C)	9.61	15.2	8.89	9.11
Dn	(589nm,20°C)	0.1851	0.201	0.207	0.217
n_o	(589nm,20°C)	1.5230	1.529	1.521	1.527

BDH Ltd.   Liquid Crystals

Merck House, Poole, Dorset, BH15 1TD England.
Tel. (0202) 669700; Telex 41186 and 418123 TETRA G; Fax (0202) 666530

Licrilite®   LC-mixture for matrix-embedded nematic microdroplets

TL212
TFT Mixture for Peregrine

Properties:

(handwritten, vertical, right margin:) ROCHE TN0510

Melting point	Not Frozen		*SAME*
S → N	<−20	°C	
Clearing point	73	°C	*66*
Viscosity	η	+20 °C	32	cSt	*34 (22°)*
Dielectric anisotropy $\Delta\varepsilon$ 1 kHz, 20 °C	10.1		*16.5*
$\varepsilon_\parallel$ 1 kHz, 20 °C	14.5		*22.6*
$\varepsilon_\perp$ 1 kHz, 20 °C	4.4		*6.1*
Optical anisotropy Δn	0.1833		*0.193*
(20 °C, 589 nm) n_o	1.5159		*1.520*
n_e	1.6992		*1.719*

Multiplex properties measured at 90° twist
V(90,0,20) (Saturation)	–	V
V(10,0,20) (Threshold)	–	V

Elastic constants	K_1	+20 °C	–	10^{-12} N
	K_3	+20 °C	–	10^{-12} N
	K_3/K_1	+20 °C	–	

APPENDIX D   GEL PERMEATION ANALYSIS

Gel Permeation Analysis   Peregrine Optifilm

Apodized Chromatogram for Sample 82-3
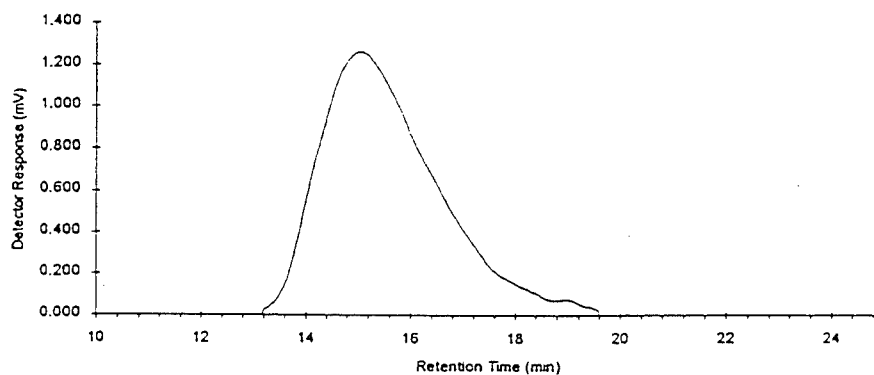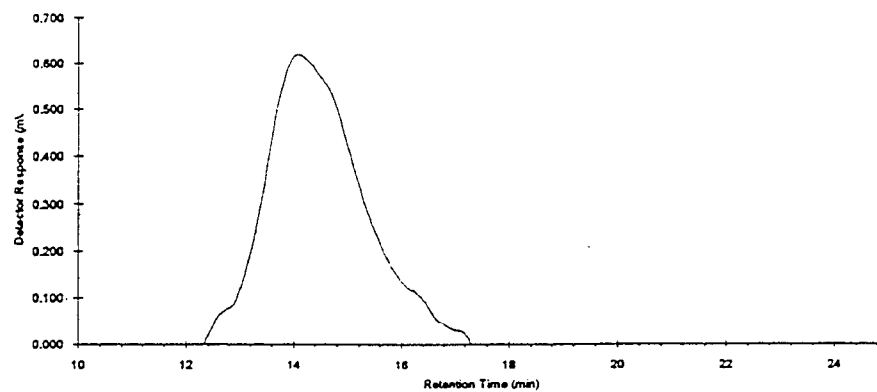

Molecular Weight Plot Sample 82-3
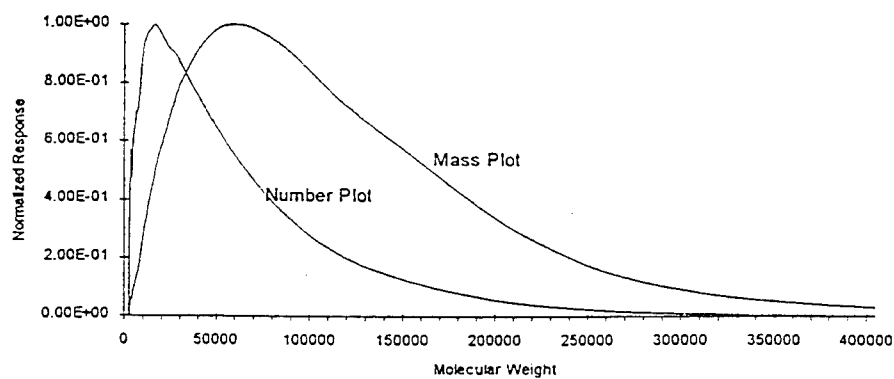
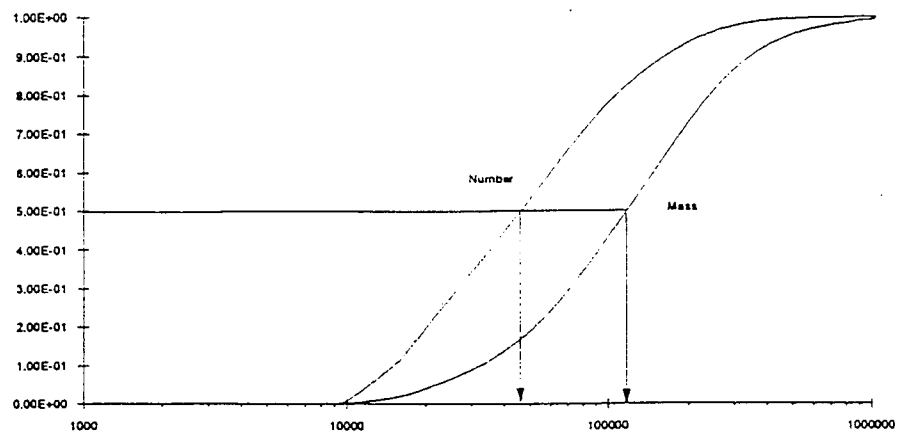Cumulative Mw and Mn Plot Sample 82-3
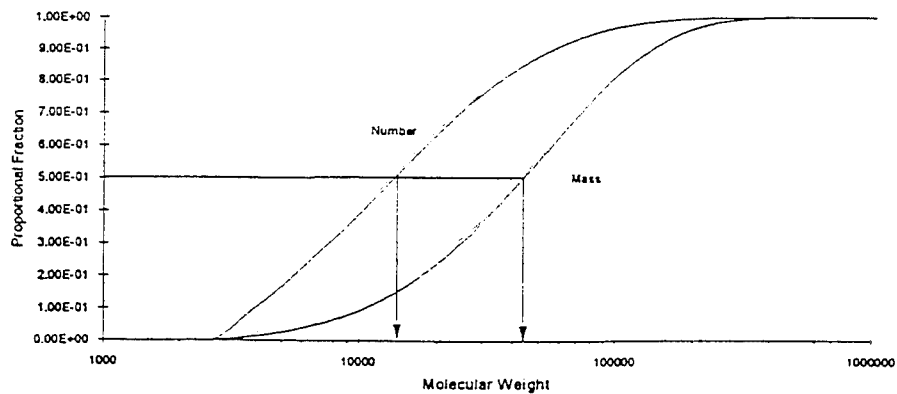
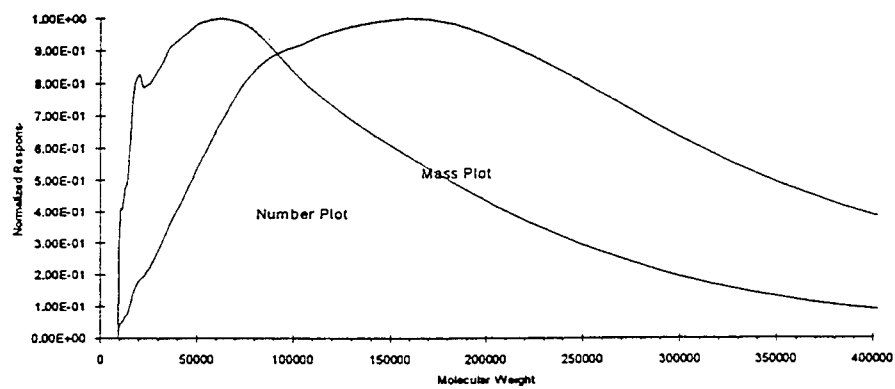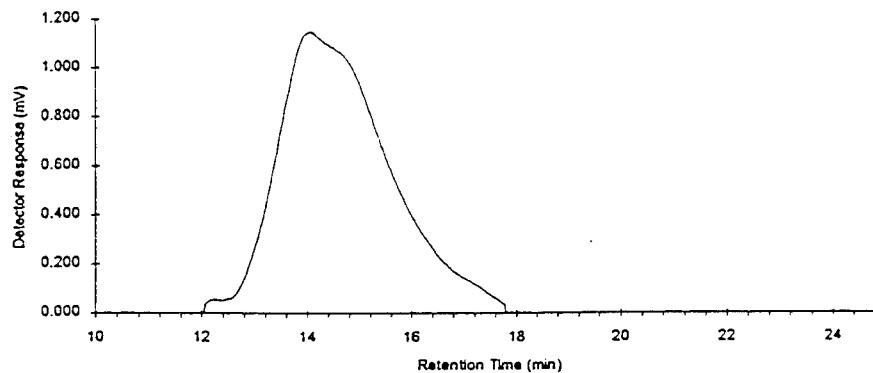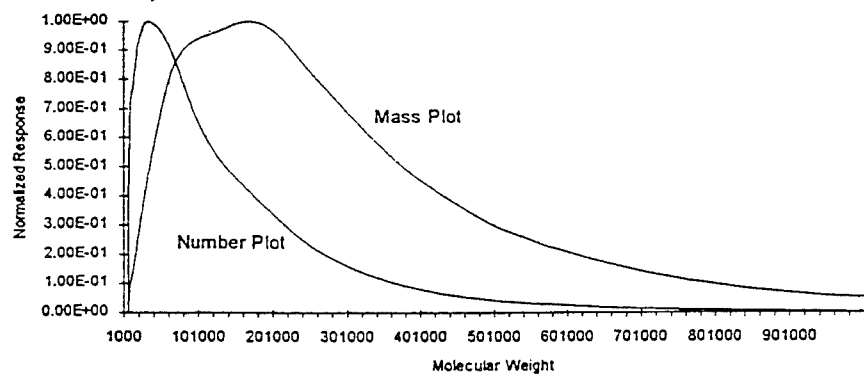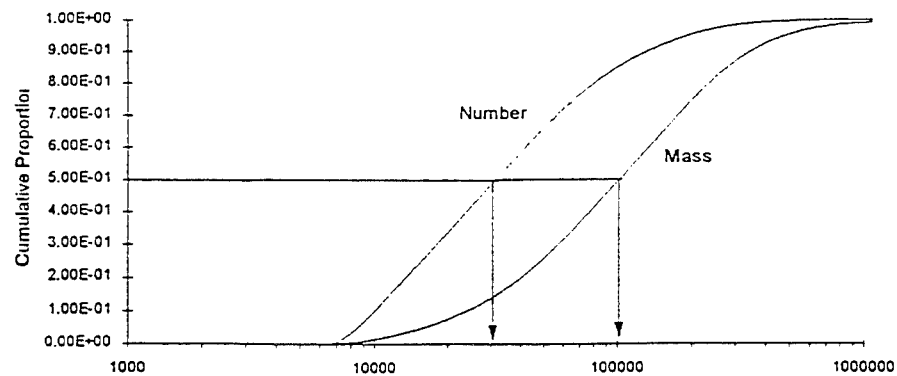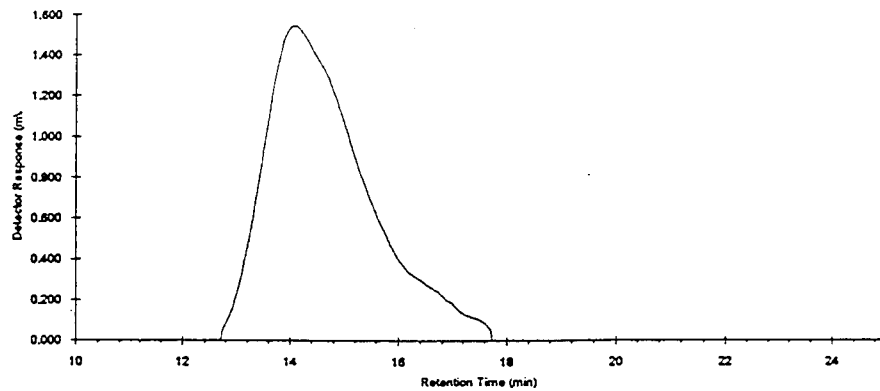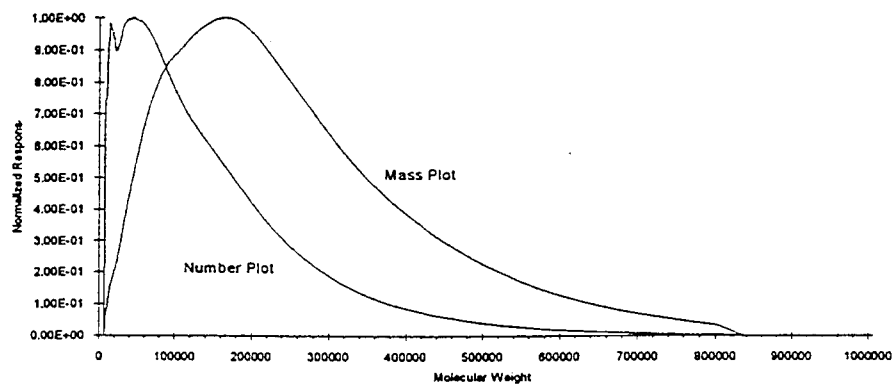# Gel Permeation Analysis   Peregrine Optifilm

Apodized Chromatogram for Sample 93-16

Molecular Weight Plot Sample 93-16

Apodized Chromatogram for Sample 93-21

Molecular Weight Plot Sample 93-21

Cumulative Mw and Mn Plot Sample 93-21

Apodized Chromatogram for Sample 93-09

Molecular Weight Plot Sample 93-09

Cumulative Mw and Mn Plot Sample 93-09